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RECOMMENDED METHODS OF REDUCTION, NEUTRALIZATION,
RECOVERY, OR DISPOSAL OF HAZARDOUS WASTE

VOLUME IV. DISPOSAL PROCESS DESCRIPTIONS,
BIOLOGICAL AND MISCELLANEOUS WASTE TREATMENT
PROCESSES

TRW SYSTEMS GROUP

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

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16. Abstract: This volume provides descriptions of selected processes currently utilized for the treatment or disposal of hazardous wastes. These descriptions detail the important features of each process and discuss their applicability to the various classes of waste materials. This volume contains descriptions of four biological processes including activated sludge, aerated lagoons, oxidation ponds, and trickling filter. There are also five miscellaneous processes described including dialysis, electro-dialysis, ion exchange, reverse osmosis and radioactive waste solidification.					
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RECOMMENDED METHODS OF
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Volume IV. Disposal Process Descriptions -
Biological and Miscellaneous
Waste Treatment Processes

By

R. S. Ottinger, J. L. Blumenthal, D. F. Dal Porto,
G. I. Gruber, M. J. Santy, and C. C. Shih
TRW Systems Group
One Space Park
Redondo Beach, California 90278

Contract No. 68-03-0089
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Project Officers

Norbert B. Schomaker
Henry Johnson
Solid and Hazardous Waste Research Laboratory
National Environmental Research Center
Cincinnati, Ohio 45268

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in:

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

Under Section 212 of Public Law 91-512, the Resource Recovery Act of 1970, the U.S. Environmental Protection Agency is charged with preparing a comprehensive report and plan for the creation of a system of National Disposal Sites for the storage and disposal of hazardous wastes. The overall program is being directed jointly by the Solid and Hazardous Waste Research Laboratory, Office of Research and Development, National Environmental Research Center, Cincinnati, and the Office of Solid Waste Management Programs, Office of Hazardous Materials Control. Section 212 mandates, in part, that recommended methods of reduction, neutralization, recovery, or disposal of the materials be determined. This determination effort has been completed and prepared into this 16-volume study. The 16 volumes consist of profile reports summarizing the definition of adequate waste management and evaluation of waste management practices for over 500 hazardous materials. In addition to summarizing the definition and evaluation efforts, these reports also serve to designate a material as a candidate for a National Disposal Site, if the material meets criteria based on quantity, degree of hazard, and difficulty of disposal. Those materials which are hazardous but not designated as candidates for National Disposal Sites, are then designated as candidates for the industrial or municipal disposal sites.

A. W. Breidenbach, Ph.D., Director
National Environmental Research Center
Cincinnati, Ohio

REVIEW NOTICE

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ACTIVATED SLUDGE PROCESS

1. INTRODUCTION

The activated sludge process is a continuous process in which incoming waste water is mixed with biological growths recirculated from the final clarifier to form a mixed liquor, followed by aeration, separation of the sludge from the effluent, and subsequent return of a portion of the settled sludge to be mixed with additional waste. The activated sludge for the process is formed by the growth of micro-organisms imbedded in gelatinous matrices feeding on organic material in the waste water under aerobic conditions. These flocculent suspensions that are developed usually possess excellent settling and oxidative properties.

The conventional plug flow activated sludge process (Figure 1) is normally designed for the treatment of domestic wastes, and yields BOD* reductions up to 95 percent. The conventional system, however, has several disadvantages when industrial wastes are to be treated - including uneven distribution of biological solids and contaminants in the aeration basin and the inability to cope with shock loading. Complete mixing aeration designs[†] (Figure 2) are therefore generally considered for industrial waste water treatment. Concentration gradients are minimized and load variations are dampened in complete mixing aerators, and the resultant effluent quality is usually better than that achieved by the conventional process. Numerous modifications to the activated sludge process exist and the more important of those are described briefly in a later section.

* Biochemical oxygen demand (BOD) is the amount of oxygen required for the biological oxidation of the organic matter in waste water.

† The complete mixing activated sludge process is one in which the untreated wastes are mixed almost instantaneously throughout the entire aeration basin. Mixing is normally effected by mechanical aerators.

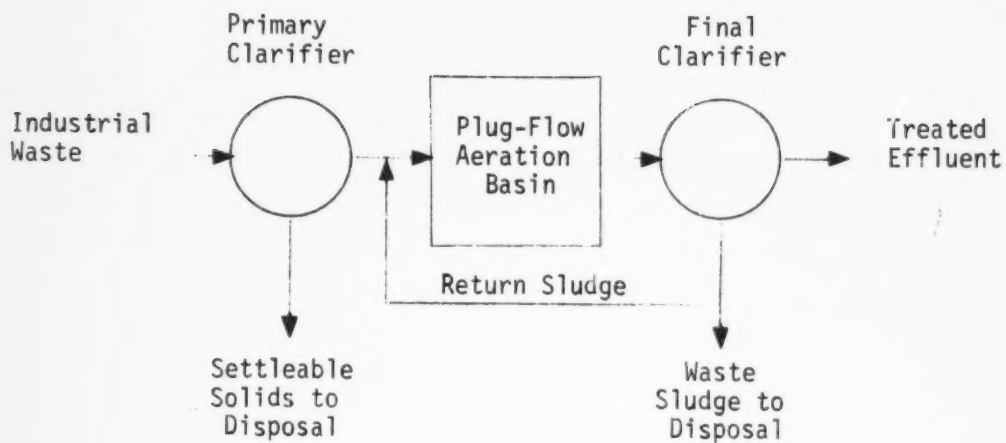


Figure 1. Conventional Activated Sludge Process

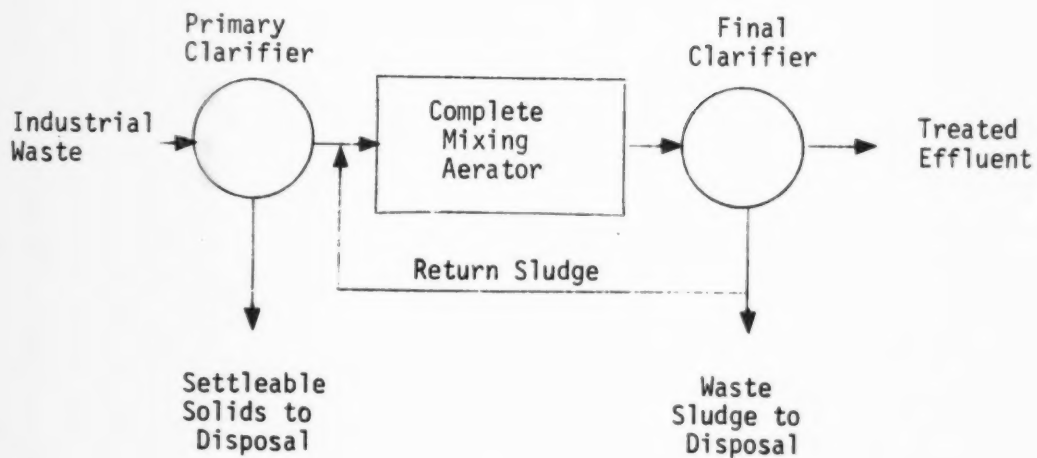


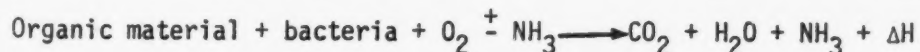
Figure 2. Complete Mixing Activated Sludge Process

2. OPERATION PRINCIPLE

The basic mechanism for removal of organic material from waste water by the activated sludge process can be represented by the three chemical reactions occurring simultaneously - energy, synthesis, and endogenous respiration. Energy and synthesis are often referred together as oxidative assimilation, and involve the consumption as food of organic material present in the waste by micro-organisms. A portion of the food is used as fuel to supply energy for metabolism while the remaining food provides building components resulting in the formation of new cellular material.

Endogenous respiration is generally considered as a maintenance mechanism of the micro-organisms, with the production of carbon dioxide, water, and ammonia. In the initial growth phases when organic food is present, endogenous respiration occurs simultaneously with the oxidative assimilation process. As the food supply diminishes, however, organic matter within the sludge is utilized and results in the endogenous growth phase.

The reactions of energy, synthesis, and endogenous respiration can be summarized in the following way:



where ΔH is the heat liberated by the reaction and is related to the energy made available for metabolic purposes.

The bacteria necessary to consume the organic material in the waste are present in the activated sludge flocs. The bacteria type depends on the characteristics of the organic matter in the waste water, although protozoa and metazoa are usually present on the surface of the flocs.

3. PROCESS DESIGN

The principle components of the activated sludge process include the following units:

- (1) Pretreatment units for screening, grit removal, and primary sedimentation of raw waste;
- (2) Diffuser or mechanical aerator;
- (3) Aeration basin;
- (4) Secondary sedimentation tank;
- (5) Sludge return pump;
- (6) Excess sludge disposal facility.

Screens are generally present in waste water treatment systems to remove large objects but they may not have any value with industrial wastes. Aerated grit removal units, however, are particularly suitable for the separation of grit from highly organic industrial wastes. Primary sedimentation tanks are used to reduce the amount of settleable solids in the waste and could lead to as much as 60 percent removal of the suspended solids and up to 35 percent BOD reduction. Because of the cost associated with sludge processing and disposal, however, primary sedimentation tanks have been eliminated in some activated sludge system.

Basically, there are two types of devices utilized to introduce air into the waste water in activated sludge systems. Diffusers generally distribute compressed air supplied by blowers to points of use in the aeration basin, and entrain the air in waste water through the use of diffusers which divide the air into fine bubbles to provide better oxygen transfer. Mechanical aerations, on the other hand, transfer atmospheric oxygen by moving the "mixed liquor"* and bringing it into contact with air, and are more widely used in treating industrial wastes because of easier maintenance. Both types

* The activated sludge when combined with the influent waste water is known as mixed liquor.

of aeration systems are designed to insure sufficient dissolved oxygen dispersed throughout the aeration basin and maintain the biological flocs in suspension, thus providing maximum contact among bacteria, waste water, and oxygen. Combinations of diffusers and mechanical aerators are sometimes used to meet high rates of oxygen demand.

The primary variables influencing the design of the activated sludge process are the influent BOD and specified effluent BOD, the rate of waste water flow, the BOD removal kinetics of the waste water, the influent volume suspended solids, the oxygen requirements, the excess sludge yield, and the settleability of the activated sludge. Other factors that enter indirectly into the design include temperature and pH levels, and the nutrient requirements, which all have a significant effect on the biological kinetics of the system.

The proper design and operation of activated sludge systems involves the balance of the relationship between the oxidation and synthesis mechanisms for removing the organic matter from the mixed liquor. For this reason, the Water Pollution Control Federation recommends the "sludge loading ratio" (SLR) as the loading parameter to be used for activated sludge. The sludge loading ratio is a measure of the food-to-micro-organisms ratio and is normally expressed in pounds of BOD per day per pound of MLVSS.* Good activated sludge operations are normally attained at organic loadings of between 0.3 and 0.7 lb BOD/day/lb MLVSS. The equation for the calculation of the SLR is:

$$SLR = \frac{24 S_a}{X_v t} \quad (1)$$

* MLSS or "mixed liquor suspended solids" is the amount of sludge solids in the mixed liquor and MLVSS or "mixed liquor volatile suspended solids" is the volatile portion of the MLSS. Both are usually expressed in mg/l and related by $MLVSS = 0.8MLSS$. MLVSS is supposedly a better representation of the active biological mass in the system. The presence of higher than nominal level of inert solids, however, could lead to MLVSS considerably less than MLSS.

where S_a is the influent BOD in mg/l, X_v is the average MLVSS concentration in the aeration basin in mg/l, and t is the aeration time in hr. Both the MLSS and the MLVSS concentrations in the aeration basin depend partly on the recycle ratio of the settled sludge. To produce good flocculation and good liquid-solid separation, minimum MLSS of 1000 mg/l are generally needed. The nominal MLSS level is between 2000 and 5000 mg/l.

Experimental programs are almost always required to develop the necessary design data for activated sludge systems. The design parameters requiring determination will become apparent in the process design equations proposed by Eckenfelder.¹²⁶³

Aeration time, t (hr)

$$t = \frac{24 S_a}{SLR \cdot X_v} \quad (2)$$

from which aeration basin volume is readily computed knowing the rate of waste water flow.

Effluent BOD, S_e (mg/l)

$$S_e = \frac{S_a}{1 + k X_v t} \quad (3)$$

where k is the biological reaction rate constant and is a strong function of the waste water characteristics and temperature. The value of k ranges from 0.00006 to 0.002 (1/mg - hr).

Excess sludge yield, ΔX_v (lb/day)

$$\Delta X_v = 8.34 Q (S_o + a (S_a - S_e) - b \frac{t}{24} \cdot X_v) \quad (4)$$

where S_o is the influent volatile suspended solids in mg/l, a is the sludge yield coefficient in lb VSS per lb of BOD removed, Q is the rate of waste water in MGD, b is the rate of sludge auto-oxidation fraction per day. The parameter a reflects the synthesis of biological solids for soluble wastes and has values ranging from 0.2 to 0.4 lb VSS per lb BOD ultimately removed from the waste. The parameter b will usually have a value of 0.20 to 0.26 per day.

Oxygen requirements, O_2 (lb/day)

$$O_2 = 8.34 Q (a' (S_a - S_e) + b' \frac{t}{24} X_v) \quad (5)$$

where a' is the oxygen utilized for growth per unit substrate removed in 1 lb O_2 per 1 lb BOD removed and b' represents the endogenous respiration rate in 1 lb O_2 1 lb VSS per day.

In addition, knowledge of the sludge volume index (SVI) of the mixed liquor from the aeration basin is necessary for good process operation. Since the ability to separate out the activated sludge depends on the rate at which the solids settle to the bottom of the secondary sedimentation tank. The SVI is volume in milliliters occupied by 1 gram (dry weight) of sludge after 30 min of settling. A good SVI is approximately 100. A sludge with a SVI of 50 is dense and compact and gives a somewhat turbid effluent. A SVI of 200 is indicative of a light fluffy sludge with poor settling characteristics that could lead to sludge bulking. To avoid bulking, the return sludge rate must be increased to maintain the solids concentration in the aeration basin.

To produce a clarified effluent with minimum solids concentration, mixed liquor from the aeration basin flows to a secondary sedimentation tank where the sludge flocs are separated from the liquid. The important parameters in the design of secondary sedimentation tanks for good sludge separation include surface overflow rate, retention time, and tank depth. Modern sedimentation systems for municipal or industrial wastes are normally designed with surface overflow rates of 800 to 1,000 gal/day/sq ft, retention time of about 2 hours, and a minimum tank depth of 10 ft.

Return sludge pumps usually have capacity up to 50 percent of the waste water flow and are normally operated at 20 to 30 percent of the waste water flow and 8,000 to 10,000 mg/l suspended solids.

Since only a portion of the settled sludge is returned to the aeration basin, the excess sludge produced in the process must be disposed of through anaerobic or aerobic digestion, dewatering, and return to the land. Vacuum filtration to remove the excess activated sludge from secondary sedimentation is usually not practiced because of the poor filtration properties of activated sludge.*

To illustrate the design and operation concepts discussed here, the detailed flow diagram of a municipal conventional activated sludge facility is shown (Figure 3).¹²⁹⁷ The waste water treatment is located at San Antonio, Texas and some of its design characteristics are:

Rated capacity = 24 MGD

Two primary clarifiers

Four 2-pass aeration tanks

Total volume of aeration = 7,750,000 gal

No reaeration

Detention time = 6.0 hr

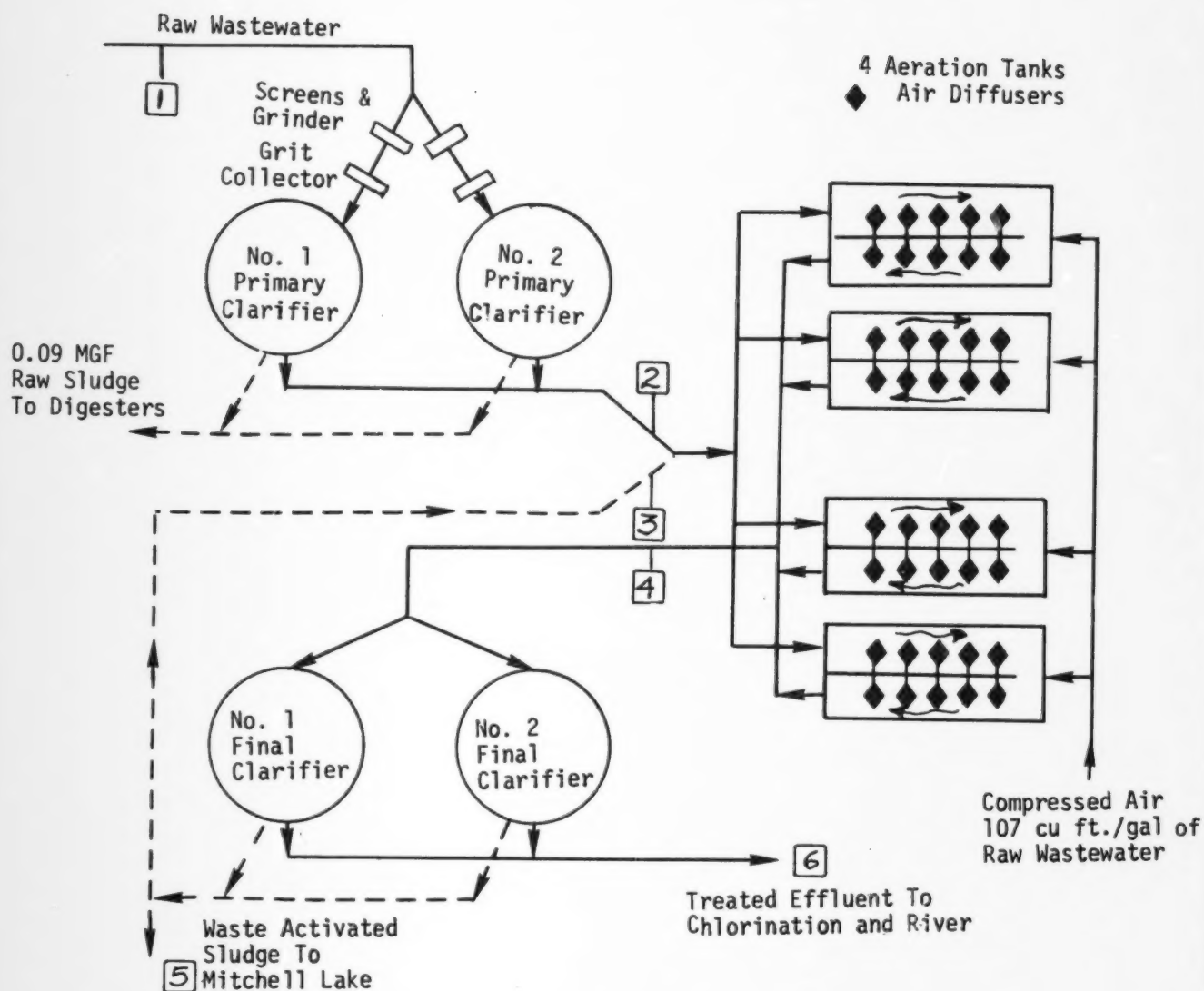
Air diffusers - ceramic tubes, 24 in.long, 3 in.diameter,
equally spaced along one side of each tank

Two final clarifiers

4. PROCESS ECONOMICS

An effective approach in estimating the capital cost of an activated sludge system is to calculate the unit costs of the major process components and add to the total direct material and field labor costs and indirect construction overhead, engineering, and contingencies. The design and cost bases of principal process components are summarized on the next page.

* A complete discussion of the sludge handling and disposal practices is obtainable from the Federal Water Pollution Control Administration.0283



Stream No.	1	2	3	4	5	6
Flow, MGD:	22.4	22.3	9.6	31.9	0.85	21.5
BOD, mg/l	221	177				27.8
Suspended Solids, mg/l:	230	122	3080	1130	3080	12.6
pH:	7.3					7.9

Figure 3. Detailed Flow Diagram* of Rilling Wastewater Treatment Plant at San Antonio, Texas

* Figure 1c of Reference 1297

<u>Process Component</u>	<u>Design Basis</u>	<u>Cost Basis</u>
Aeration equipment	Oxygen requirement	Cost/HP
Aeration basin	Waste flow rate-organic loading	Cost/volume
Secondary Sedimentation	Overflow rate	Cost/surface area
Return sludge pump	Return sludge rate	Cost/HP
Excess sludge disposal		
Sludge digestion	Excess sludge rate-digestion kinetics	Cost/volume
Thickening	Mass loading	Cost/volume
Centrifugation	Waste flow-solids loading	Cost/waste flow

The critical design parameters that indirectly determine the capital cost of activated sludge systems include the waste water flow rate, the influent and effluent BOD, the average MLVSS, and the biological reaction rate constant k . A capital cost model for the treatment of industrial wastes by the activated sludge process has been developed by Eckenfelder, 1983 and indicates the weight of each of the design parameters in determining the total capital cost of the treatment plant:

$$\text{Cost (in \$1000)} = Q^{0.69 + 0.00019S_a} (17 (S_a/S_e)^{0.76} + 215) \times (1.05 + 0.44 / (kX_v))$$

Operating costs for activated sludge systems are usually determined by waste water and return sludge pumping capacity and the power requirement of the aeration equipment and clarifiers. Operating costs could range from \$10 to \$2,000/MG of waste water treated.

5. PROCESS MODIFICATIONS

High Rate Aeration

The high rate or modified aeration process is similar to the conventional process except that higher loading factors of 2 to 5 lb BOD per day per lb MLVSS are used. Both the construction and power costs are lower, but the degree of purification is also reduced.

Tapered Aeration

This is an operational improvement of the conventional process. Since oxygen demand is relatively high at the head end of the basin due to the impact of high BOD of the influent and then decreases along the length of the basin, decreasing amounts of air are provided to match the oxygen demand. Lower power costs usually result.

Step Aeration

Step aeration involves the introduction of waste flow at intervals throughout the length of the tank (Figure 4) and should be more appropriately named "step loading". The intent is to minimize the effects of shock loading and the oxygen demand gradient.

Extended Aeration

Extended aeration processes are characterized by long aeration periods and low loading factors. The objective of the process is to reduce the quantity of excess sludge produced and to achieve uniform BOD and suspended solids concentration throughout the aeration basin. Because of the high suspended solids level in the mixed liquor and the extended length of aeration time, endogenous respiration becomes a determining factor in defining the sludge quality in the process. Effluents from this process usually contain relatively less BOD but higher suspended solids.

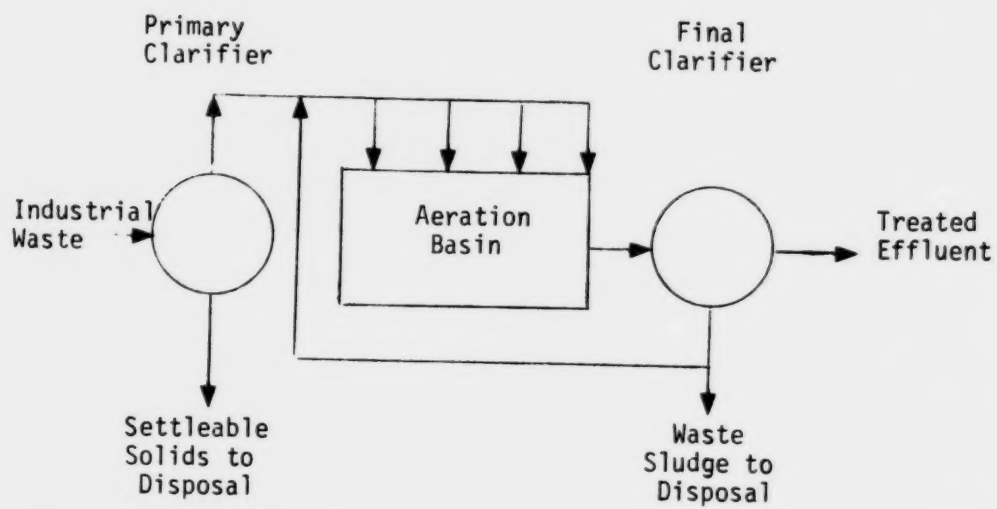


Figure 4. Step Aeration Activated Sludge Process

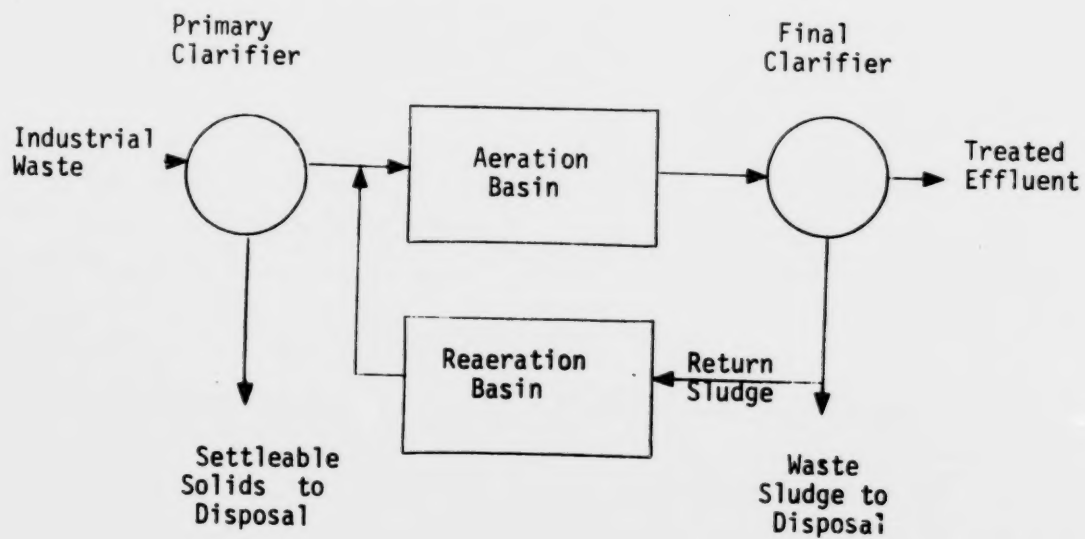


Figure 5. Contact Stabilization Activated Sludge Process

Contact Stabilization Aeration

In the contact stabilization process, the return sludge is aerated separately (Figure 5) until hydrolysis and conversion to cells is complete. The sludge flocs thus produced have a higher capability of removing substrate BOD when finally discharged into the main aeration basin. The process has an actual contact between waste water and mixed liquor of 30 min to 1 hr, and is completely inapplicable to wastes containing a high fraction of soluble organics.

A summary (Table 1) of some of the differences in loading parameters among variations of the activated sludge processes has been presented by Genetelli.¹²⁶⁶

6. PROCESS APPLICABILITY

The complete mixing activated sludge process has been applied very extensively in the treatment of refinery, petrochemical, and biodegradable organic waste waters. In order to avoid adverse effects on the system, pretreatment to remove certain materials from the waste water are often necessary. Some materials present could interfere with the treatment process or be toxic to the bacteria in the sludge, and some limits must be placed on the amount permissible in the waste water. Maximum limits for selected waste water characteristics (Table 2) are given by Jones⁰⁵³⁴ and Klein.⁰⁶⁶⁹

In addition, strongly acidic or alkaline wastes must be neutralized to pH limits between 5 and 9 before discharge to the activated sludge system. Temperature should not exceed 110 F for good operation because of lower oxygen solubility, and essential nutrients of ammonia and phosphorus must be supplemented if these are not originally present in the industrial waste water.

TABLE 1
LOADING PARAMETERS FOR ACTIVATED SLUDGE PROCESSES

Activated Sludge Process	Sludge Loading Ratio lb BOD/Day/lb MLVSS	Volumetric Loading lb BOD/ Day/1000 ft ³ of Aeration Tank Capacity
Conventional	0.2 - 0.7	35
Complete Mixing	0.2 - 0.7	50
High-Rate Aeration	2 - 5	100
Tapered Aeration	0.2 - 0.7	35
Step Aeration	0.2 - 0.7	50
Extended Aeration	0.05- 0.2	20
Contact Stabilization	0.2 - 0.7	70

TABLE 2
 MAXIMUM PERMISSIBLE LEVEL OF WASTE WATER CHARACTERISTICS
 FOR BIOLOGICAL TREATMENT 0534,0669

Characteristics	Maximum Permissible Level
Oil and Grease	75 mg/l
Nonbiodegradable Suspended Solids	125 mg/l
Sulfides	250 mg/l
Cyanides	1 ppm
Arsenic	0.2 ppm
Antimony	0.2 ppm
Cadmium	2.0 ppm
Chromium	0.5 ppm
Copper	0.2 ppm
Lead	1 ppm
Mercury	0.07ppm
Nickel	1 ppm
Silver	0.03 ppm
Zinc	5 ppm

The activated sludge process is generally applied where a high degree of BOD removal is required and where suitable land is not available. Organic wastes that have been successfully handled by the process include the following: acetaldehyde, acetic acid, acetone, acrolein, high boiling alcohols, ethyl alcohol, formaldehyde, formic acid, glycerol, glycols, isobutyl alcohol, isopropyl alcohol, methanol, and phenolics. A summary by Jones (Table 3)* of activated sludge plants treating petrochemical and organic wastes indicates the representative types of mixed wastes that could be treated by the activated sludge process along with the effluent quality obtained. The typical BOD removal efficiencies are in the 90 to 95 percent range.

It has been claimed that toxic metals in waste water could be largely removed by sedimentation and biological filtration in the activated sludge process.[†] However, biological treatment by activated sludge does not produce a metal free final effluent and in fact, toxic quantities of the metals may still be present in the effluents. The approximate amounts removed by the process are : Cr, 70 percent; Ni, 30 percent; Zn, 60 percent; Pb, 90 percent; Cu, 80 percent.⁰⁶⁶⁹

Although the activated sludge process is probably not applicable to the direct treatment of hazardous wastes in National Disposal Sites, installation of the process with a proper analytical monitoring system is recommended for treating all the process waste water (spent cleaning solutions, incinerator scrubber waste liquor, and cooling water) generated within the National Disposal Sites to ensure no release of pollutants to the environment. The activated sludge process is most adaptable for treating biodegradable organic wastes with influent BOD₅ less than 3000 mg/l. Due to the sensitivity of the process to surges in waste loads, however, it is recommended that the process waste water be partially pretreated in trickling filters to stabilize the reaction of the activated sludge process to surges in loading.

* Table 40 0534

† The influent level of these metals must be below the maximum limits indicated in Table 2.

TABLE 3
ACTIVATED SLUDGE TREATMENT OF INDUSTRIAL
ORGANIC WASTES

Product and/or Process	Flow (MGD)	BOD			COD			Organic Loading lb BOD ₅ /day (lb MLSS)	Nutrients Reqd.	Remarks
		In (mg/l)	Out (mg/l)	Rem (%)	In (mg/l)	Out (mg/l)	Rem (%)			
Refinery, Natural Gas Liquids, Chemical Specialties, Sanitary Sewage	4.87	90	20	78	200	90	55	0.1	None	Effl. phenol 0.05 Effl. oil 0.5 mg/l
Phthalic Anhydride, Phenol, Salicylic Acid, Rubber Chem., Aspirin, Phenacetin	2.54	45.7	6.1	86.7				0.031	None	Brush Aeration, treats trickling filter effluent, 55% sludge return
Refinery, Detergent Alkylate	2.45	345	50-100	71-85.5	855	150-200	76.6-82.5	0.08	PO ₄	Phenols in = 160 mg/l Sulfide in = 150 mg/l Lab scale
Butadiene Maleic Acid	2.0	2,000	25	98.8	2,990	480	84	0.24	NH ₃	
Butadiene Alkylate	1.5	1,960	24	98.8	2,980	477	98.3			
Butadiene, Maleic Anhydride, Fumaric Acid, Tetrahydrophthalic Anhydride, Butylene Isomers, Alkylate	1.5	1,960	24	98.8	2,980	51	84	0.24 (MLVSS)	NH ₃	Surface aerators wastes contain: alcohols, maleic acid, fumaric acid, acetic acid, C ₁ -C ₆ aldehydes, furfural, water soluble addition products
Ethylene Propylene, Benzene	1.44	600	90	85	700	105	85		None	Oil waters: C ₆ -C ₁₀ oils 90% phenol removal
Naphthalene, Butadiene, Phenol, Acrylonitrile, Soft Detergent Bases, Resins, Other Aromatics	0.43	500	60	85-90	600	90	80-85	1.5	NH ₃ PO ₄	Sour waters: Oil in = 500 mg/l Phenol in = 65 mg/l pH adjustment, preceded by trickling filter, phenol removal = 99.9%
Phenol, 2,4-D Aniline, Nitro-Benzene, Rubber Chem., Polyester Resins, Misc. Chem.	0.97	370	76	76.2				0.4	NH ₃ PO ₄	Accelerator Pilot Plant Sewage added in ratio 1:600 once a week
Ethylene, Propylene, Butadiene, Benzene, Polyethylene, Fuel Oils	0.63	85	10	99	200	75	62.5			Quench waters, polyethylene and benzene wastes: preceded by trickling filter, effl. phenol 0.01 ppm
Refining Processes	0.51-0.63	125	15-25	80-88			65-80	0.28-0.4	PO ₄	Phenol removal 85-94%; Oil removal 75-85%; Effl. phenol 0.5 mg/l; Effl. oil 1-2 mg/l; Temp. = 30°C
Nylon	0.4	1,540	250	83.8						
Petroleum Products	0.27	440	5	98.8	500	60	88			Phenol in = 25 ppm Phenol out = 1 ppm
Acrylic Fibers	0.252	2,260	118-226	90-95				0.4		Wastes contain acrylonitrile, dimethylamine, dimethylformamide, formic acid temp. 35-37°C return sludge 10-50% mechanical aeration
Acetone, Phenol p-Cresol, Diethyl-, Butyl-p-Cresol, Dicumyl Peroxide	0.216	3,560-4,400	1,030-750	71-83				0.89-1.1		Waste phenol 600 ppm Waste BOD 7,500-8,000 Waste diluted w/ effl. or water; pilot plant
Resins-Formalin, Acrylonitrile, Phenol-Formal., Epoxy Resins, Textile Aux.	0.2	890	444-266		50-70			0.8-1.2		Diffused-air, domestic waste added; trickling filter follows 100% recycle sludge

TABLE 3
ACTIVATED SLUDGE TREATMENT OF INDUSTRIAL
ORGANIC WASTES
(Continued)

Product and/or Process	Flow (MGD)	BOD			COD			lb BOD ₅ /day lb MLSS	Nutrients Reqd.	Remarks
		In (mg/l)	Out (mg/l)	Rem (%)	In (mg/l)	Out (mg/l)	Rem (%)			
Ethylene and Propylene Oxides, Glycols, Morpholines, Ethylene-Diamines, Ethers, Piperazine	0.15	1,950	20	99	7,970-8,340	5,120-5,950	25-40	0.51	None	Lab Scale; extended aeration; high non-biodegradable fraction followed by stab. ponds
2,4-D 2,4,5-T (Acid Wash Wastes)	0.1	1,670	125	92.5	2,500	500	80	0.78 (MLVSS)	NH ₃ PO ₄	1:1 mixture of acid wash streams diluted 9:1 prior to treatment to reduced chlorides, toxicity Lab Scale
Cracking, Isomerization of butane and Saphrene, Alkylation, Benzene, Toluene, Alcohols, ketones, Cresylic Acids	1,100	55-110	90-95					0.5		90-95% phenol removed; Lab Scale
Ethylene, Acetylene			20					0.23-0.33	PO ₄	Effl. phenol 0.1 mg/l Effl. oil 1 ppm
Nylon Manuf.-Adipic Acid			95			85		1.0-3.0	PO ₄ NH ₃	NH ₃ OH used as nutrient and neutralizing agent waste diluted 2:1
Aik. Organics										

Nomenclature

- a = sludge yield coefficient
 a' = oxygen utilized for growth per unit substrate removed
 b = rate of sludge a to-oxidation fraction per day, day^{-1}
 b' = endogenous respiration rate, day^{-1}
 k = biological reaction rate constant, $1/\text{mg-hr}$
 Q = rate of waste water flow, MGD
 S_o = influent volatile suspended solids, mg/l
 S_a = influent BOD, mg/l
 S_e = soluble effluent BOD, mg/l
 t = aeration time, hour
 X_v = average mixed liquor volatile suspended solids, mg/l
 ΔX_v = excess sludge yield, lb/day

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AERATED LAGOONS

1. INTRODUCTION

An aerated lagoon is generally defined as a basin of significant depth (usually 6 to 17 ft), in which organic waste stabilization is accomplished by a dispersed biological growth system, and where oxygenation is provided by mechanical or diffused aeration equipment.

There are two distinctly different types of aerated lagoons--the aerobic lagoon and the aerobic-anaerobic or facultative lagoon. The aerobic lagoon is designed with sufficient power input to create a turbulence level high enough to maintain the solids in suspension. Aerators must be selected not only to deliver the required oxygenation capacity but also to induce eddies near the bottom of the basin to prevent sludge deposition.

The aerobic-anaerobic or facultative lagoon is designed with only sufficient power input to maintain turbulence levels adequate to insure uniform dissolved oxygen distribution throughout the basin. The major portion of the solids are not in suspension but settle to the bottom of the basin where they undergo anaerobic decomposition. A separate sedimentation area or clarifier is sometimes included to produce a more clarified effluent.

Aerated lagoons are a relatively new innovation in the waste water treatment field. The aerated lagoon was originally developed as an attempt to increase the BOD removal capacity of existing waste stabilization ponds (oxidation ponds) by artificial aeration. More recently, aerated lagoons are being used successfully to meet the needs of higher degrees of treatment without the high construction costs associated with an activated sludge plant.

2. OPERATION PRINCIPLE

Biologically, the aerated lagoons resemble the activated sludge processes in that the typical activated sludge floc (e.g., protozoa) is invariably present and responsible for the biological removal of organic matter present in the waste. In effect, with aerobic lagoon is analogous to the extended activated sludge process with no sludge return. Due to the dispersed nature of the culture, however, aerated lagoon systems do not require close control over variations in temperature, pH, and organic loading.

Facultative lagoons employ aerobic biochemical oxidation near the surface and anaerobic decomposition of organic matter in bottom of the basin. In the absence of dissolved elemental oxygen at the bottom of the pond, breakdown of organic molecules is normally considered as a two-stage process. The complex organic molecules are first biologically converted to low molecular weight organic fatty acids by the action of acid forming facultative and anaerobic bacteria. The amounts of energy released for growth during the initial conversions are relatively small so that only a small portion of the waste is converted to new bacteria cells. The small quantities of bacterial growth minimizes the problems of biological sludge disposal.

Real waste stabilization occurs in the second stage of an anaerobic process, where organic acids are converted by specific strictly anaerobic micro-organisms into carbon dioxide and methane. The most important of the methane forming bacteria live on acetic and propionic acids, and require retention times of four days or longer for their growth.

When nitrogenous materials are also present in the waste water, these may be converted to ammonia at the same time complex organic compounds are converted into volatile acids, so that the volatile acids would be neutralized upon formation. Under these circumstances, waste stabilization occurs without methane formation.

3. PROCESS DESIGN

An aerated lagoon is usually an earthen basin with some protection near the bank for wave action caused by the aeration device. The aeration equipment used to provide uniform dissolved oxygen dispersion and mixing can either be a mechanical or diffused aerator. The effluent normally is removed without sludge separation, although clarification can be provided after the aeration basin.

The basis of design for the aerobic lagoon is quite different from that of the facultative lagoon. For this reason, the process designs of the two types of aerated lagoons will be discussed separately here.

Aerobic Lagoon

The design of the aerobic lagoon depends on the following variables: rate of waste water flow, influent and specified soluble effluent BOD, influent volatile suspended solids, the lagoon temperature and other experimentally determined parameters characterizing the waste. The following process design equations for the aerobic lagoon have been proposed by Eckenfelder.¹²⁶⁸

(i) Aeration time or sludge age, t (hr)

$$t = \frac{S_a - S_e}{k S_e [S_0 + a (S_a - S_e)] - \frac{b}{24} (S_a - S_e)} \quad (1)$$

where S_a is the influent BOD in mg/l, S_e is the specified soluble effluent BOD in mg/l, S_0 is the influent volatile suspended solids in mg/l, k is the biological reaction rate constant in (1/mg-hr), a is the sludge yield coefficient in lb volatile suspended solids (VSS) per lb of BOD removed, and b is the rate of sludge auto-oxidation fraction per day. The parameters k , a , and b are to be obtained from laboratory studies. The usual range of these parameters are: k , 0.00006 to 0.002 (1/mg-hr); a , 0.2 to 0.4 lb VSS per lb of BOD removed; b , 0.2 to 0.26 per day.

Volume of the aerobic lagoon is readily computed knowing the rate of waste water flow. The effect of lagoon temperature is taken into account as:

$$k_T = k_{20} 1.035^{T-20} \quad (2)$$

where k_T is the biological reaction rate constant at $T^\circ\text{C}$.

(ii) Volatile suspended solids, X_v , (mg/l)

$$X_v = \frac{S_0 + a(S_a - S_e)}{1 + b \frac{t}{24}} \quad (3)$$

The total suspended solids in the lagoon, X_a in (mg/l), will be approximately equal to $1.25 X_v$. X_a is also the total suspended solids in the lagoon effluent.

(iii) Total effluent BOD, S_T (mg/l)

The BOD of the effluent from lagoon systems with a high solids carry-over will be contributed by both the soluble organics remaining and the oxygen demand exerted by biological solids in the effluent. The BOD due to the solids depend on the sludge age and on the total suspended solids present in the effluent. The fraction of solids which are actually biological f is related to the sludge age t obtained from equation (1), (Figure 1) and the total effluent BOD S_T is given by:

$$S_T = S_e + f X_a \quad (4)$$

Facultative Lagoon

The effluent solid levels in facultative lagoons depend on the influent BOD and suspended solids, the aeration power level, and the mixing intensity. Field experience has indicated that the normal range of volatile solids level X_v is from 50 to 100 mg/l. The design of the facultative lagoon is based on the influent BOD and specified soluble effluent BOD, the biological reaction rate constant k , and a knowledge of X_v .

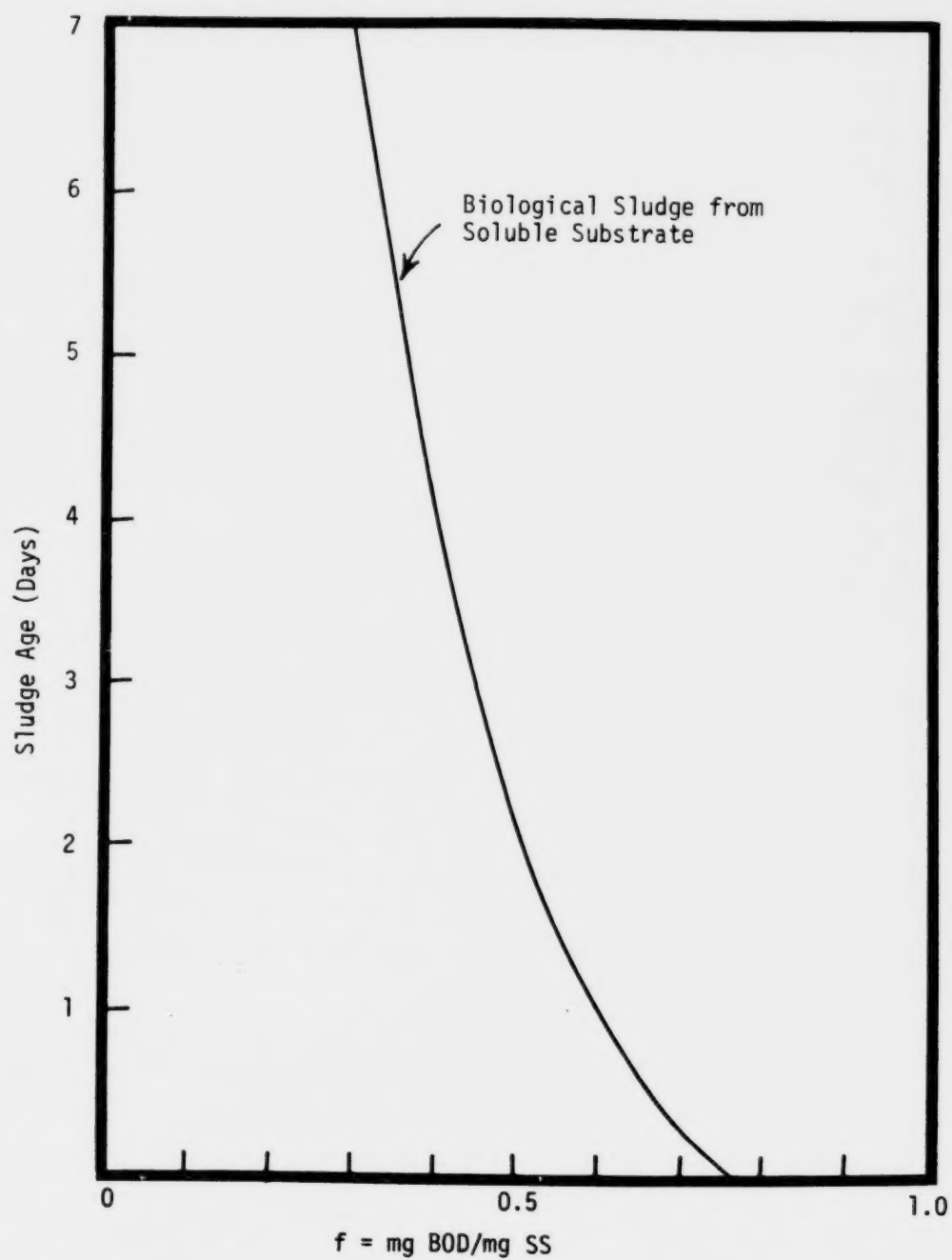


Figure 1. BOD Characteristics of Biological Sludges

(i) Aeration time or sludge age, t (hr.)

$$t = \frac{S_a - S_e}{k X_v S_e} \quad (5)$$

The effect of the lower volatile suspended solids in the facultative lagoon is that the sludge age is usually longer and a large aeration basin is required. On the other other hand, the lower volatile suspended solids level also leads to higher degree of BOD removal and a lesser problem of solids disposal. The effect of lagoon temperature is taken into account by:

$$k_T = k_{20} 1.085^{T-20} \quad (6)$$

The large value of the temperature coefficient (1.085) indicates the sensitivity of the facultative lagoon to temperature changes, and designs based on summer lagoon temperatures cannot be depended on to produce high quality effluents during the winter months.

(ii) Total Effluent BOD, S_T

The total effluent BOD is again composed of both the soluble BOD remaining and the BOD contributed by the suspended solids, and is obtained by using equation (4) and the sludge age--biological suspended solids relationship (Figure 1).

The oxygen requirements of both the aerobic and the facultative lagoon is obtained from the following equation:

$$O_2 = 8.34 Q (a' (S_a - S_e) + b' \frac{t}{24} X_v) \quad (7)$$

where O_2 is given in lb/day, a' is the oxygen utilized for growth per unit substrate removed in lb O_2 per lb BOD removed, and b' is the endogenous respiration rate in lb O_2 per lb VSS per day.

In addition to providing sufficient oxygen and uniform oxygen dispersion, minimum power levels to maintain solids in suspension are required for aerobic lagoon systems. This means minimum basin bottom velocities of 0.4 to 0.5 ft per second to prevent sludge deposition and a power level in the order of 30 to 100 HP per million gallons of basin volume for surface aerators. For facultative lagoons, the power levels needed are much lower and only in the order of 15 to 20 HP per million gallons of basin volume.

4. PROCESS ECONOMICS

The capital investment costs of an aerated lagoon system are determined by the volume of the basin and the aeration equipment required, and range from \$0.2MM for a 5 million gallon aeration basin to \$2 MM for a 100 million gallon aeration basin,⁰⁵³⁴ when land values are not included. Approximate land requirements for aerated lagoons are 8 to 16 acres per million gallon per day.

Operating costs for aerated lagoons are usually determined by the waste water pumping cost and the power requirement for the aeration equipment. Operating costs could range from \$30 to \$1,200 per million gallon of waste treated.

As to be expected, the capital and operating costs of an aerated lagoon are intermediate between those of an oxidation pond and an activated sludge unit.

5. PROCESS MODIFICATIONS

An aerated lagoon is quite simple consisting of only an aeration device in a basin. The two principal types of aerated lagoons--the aerobic lagoon and the facultative lagoon have already been described in the previous sections. Physical shapes of aerated lagoons are usually dictated by the size and shape of the land available.

6. PROCESS APPLICABILITY

Aerated lagoons have been used successfully as an economical means to treat industrial wastes where high quality effluents are not required. In most cases, aerated lagoons are being considered as an addition or modification of existing waste stabilization ponds or as an interim treatment process which can later be converted to an activated sludge system.

The main advantages of aerated lagoon systems include equalization of shock loads due to the dispersed nature of the culture, no floc dispersion or bulking problems and relatively low capital and operating costs. The main disadvantages are maximum of 80 percent BOD removal and a turbid effluent, and inactivity at low temperatures during winter months.

The removal of individual organic pollutants from waste water by aerated lagoons have been studied,¹⁴²⁴ and the typical range of reduction (after 4 hr of secondary settling) have been computed for some specific chemicals (Table 1). It must be pointed out, however, that the system operated under conditions of either oxygen starvation or cold-temperature inhibition during most of the period of data gathering, and thus the reduction indicated is influenced to some degree by competition. It is conceivable that the biological reduction for some of these chemicals could be considerably enhanced under more favorable conditions.

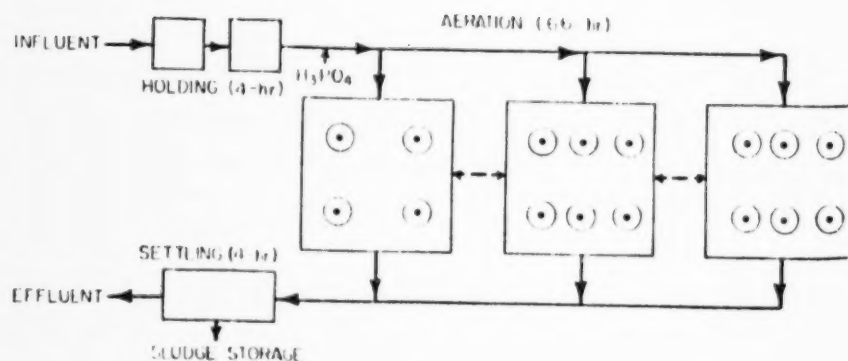
Aerated lagoons have been shown to be useful in the treatment of textile wastes, pulp and paper mill wastes, and cannery wastes, where BOD reductions of 60 to 80 percent were obtained. More recently, aerated lagoon systems have proven to be quite successful in treating synthetic organic wastes and refinery-petrochemical wastes. A layout of the aerated stabilization facility at the Institute Plant of Union Carbide is reproduced here, along with some typical operating data (Figure 2). The facility treats a waste flow of 5.3 MGD of fairly concentrated waste water (average BOD of 2100 mg/l) from a plant manufacturing several hundred organic products and intermediates, including many hazardous waste materials under consideration in this program. The key unit operations of the treatment facility are 4-hr preliminary

TABLE 1
CHROMATOGRAPHICALLY MEASURED CHEMICAL REDUCTIONS AT UNION
CARBIDE INSTITUTE PLANT'S AERATED STABILIZATION FACILITY

Percent Reduction of Compound	Compounds in Category
0-10	Ammonia Acetophenone* Ethylene Cyanohydrin*
10-30	Acetone Methyl ethyl pyridine
30-50	Ethylbutanol 2-Ethylhexanol Methanol Paraldehyde
50-70	Acrylic and butyric acids Diethylphthalate Phenyl methyl carbinol
70-90	Acetaldehyde Acetic Acid Acrylonitrile Butanol Ethanol Hexanol Isopropanol Isopropyl ether Naphthalene Styrene Toluene
90-100	Benzene Benzoic Acid Crotonaldehyde Ethyl acetate Ethyl acrylate Ethyl benzene 2-Ethylhexyl acrylate Heptane

*Possible biological intermediates.

Note: Removals were limited seasonally by either oxygen availability or cold temperature.



Average Operating Data

Variable	Summer	Winter
Temperature (°C)	35	15
DO (mg/l)	nil	20
Power (bhp/1,000 gal)	0.077	0.062
Detention time (days)	2.9	2.3
BOD load (lb/day/1,000 cu ft.)	46	56
BOD removal eff. (%)	54	48
BOD removal (lb/day)	48,000	52,000
COD load (lb/day/1,000 cu ft.)	97	113
COD removal eff. (%)	41	39
COD removal (lb/day)	78,000	86,000
Specific chemical load (lb/day/1,000 cu ft.)	42	44
Specific chemical removal eff. (%)	62	59
Specific chemical removal (lb/day)	51,000	51,000

Figure 2. Aerated Stabilization System for Treating Synthetic Organics at Union Carbide's Institute Plant

holding, 66-hr aeration, and 4-hr secondary settling with provisions for the parallel or series operation of the three aeration basins. Each aeration basin has a 17-ft water depth, a 1.3-acre surface, and a holding capacity of 4.8 million gallons.

A summary of reported data from the aerated lagoon treatment of petrochemical and refinery waste water has been compiled (Table 2). Additional treatment of effluents from aerated lagoons in waste stabilization ponds prior to release have become quite common practice.

The limitations on the BOD removal efficiency will probably circumvent the use of aerated lagoons as a single waste treatment unit where high quality effluents are specified. At a National Disposal Site for handling hazardous wastes, it is recommended that the installation of aerated lagoons be considered only under the following circumstances:

- (1) as an interim treatment process that will be later converted to an activated sludge unit or;
- (2) as an "equalization tank" preceding other treatment units in a multistage biological treatment facility or;
- (3) as a "polishing pond" following other treatment units in a multi stage biological treatment facility.

TABLE 2
AERATED LAGOON TREATMENT OF PETROCHEMICAL WASTES*

Product and/or Process	Flow (MGD)	BOD			COD			Organic Loading lb BOD/Acre day	Nutrients Reqd.	Remarks
		In (mg/l)	Out (mg/l)	Rem %	In (mg/l)	Out (mg/l)	Rem %			
Refinery Butadiene, Butyl Rubber	19.1	225	100	55	610	350	43	4,630	P ₀₄	Followed by stab. pond temp - 32 C 30% COD is non-bio-degradable Lab Scale
Refinery, Detergent Alkylate	2.45	345	50-100	71-85	855	150-200	77-83	6,300	P ₀₄	Influent phenols 160 mg/l Influent sulfides 150 mg/l Lab Scale
Cyclohexane, p-Xylene, Benzene, Paraffinic Naphtha, o-Xylene Gasoline Nylon Fibers	0.51	100	25	75				400		Surface aeration, Waste is extensively pretreated. Followed by pond
Chemicals for Lubricating oils	0.2	465	180	61	1,050	600	43			

* Table 42 of Reference 0534

NOMENCLATURE

- a = sludge yield coefficient
- a' = oxygen utilized for growth per unit substrate removed
- b = rate of sludge auto oxidation fraction per day, day⁻¹
- b' = endogenous respiration rate, day⁻¹
- f = fraction of suspended solids which are actually biological
- k = biological reaction rate constant, l/mg-hr
- Q = rate of waste water flow, MGD
- S_a = influent BOD, mg/l
- S_e = soluble effluent BOD, mg/l
- S_o = influent volatile suspended solids, mg/l
- S_T = total effluent BOD, mg/l
- t = aeration time or sludge age, hr.
- T = lagoon temperature, °C
- X_a = total suspended solids in lagoon, mg/l
- X_v = volatile suspended solids in lagoon, mg/l

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OXIDATION PONDS

1. INTRODUCTION

Oxidation ponds are large shallow basins which depend on algal photosynthesis and natural surface reaeration for the oxygen used in treating biodegradable wastes. In the treatment of industrial wastes, oxidation ponds are best used to polish the effluents from other biological waste treatment processes, although in some instances they have also been used to treat entire plant wastes. Oxidation ponds have been widely used where land is plentiful and climate conditions are favorable.

The optimum depth of oxidation ponds is about 4 ft, for aerobic conditions to prevail. In heavily loaded ponds and in the bottom muds of relatively deep ponds, a certain amount of waste stabilization will occur anaerobically. Anaerobic treatment for industrial wastes, however, has been generally unsatisfactory and usually limited to meat industry wastes.

Retention times in oxidation ponds range from a few days up to 3 months, depending on the nature and composition of the waste, and the environmental conditions present during treatment. Oxidation ponds require a minimum of maintenance, but some control is desirable to ensure proper algae growth throughout the depth of the basin. Multiple ponds in series are sometimes used to minimize short-circuiting of flow.

2. OPERATION PRINCIPLE

Fundamentally, the oxidation pond utilizes bacteria to aerobically stabilize the organic material present in the waste water, resulting in the oxidation of carbon to carbon dioxide, hydrogen to water, and nitrogen to ammonia. The oxygen for the bacteria is supplied by both air surface transfer and the metabolism of algae in the pond. The cycle is completed when the algae use the waste stabilization products carbon dioxide and ammonia to synthesize new cells in the presence of sunlight, and thereby

liberate oxygen as an end product to be used by the bacteria for oxidizing the organic waste and synthesizing bacterial protoplasm. The important relationship responsible for organic waste stabilization in the oxidation pond is the relatively slow rate of degradation of cellular protoplasm as compared to the rate of degradation of organic matter for the synthesis of cellular protoplasm.

In addition to biological stabilization, other processes taking place in oxidation ponds may include balancing of the acids, coagulation and sedimentation, neutralization of any alkalinity by carbon dioxide from the air and produced by oxidation of organic matter. The net effect of these is a possible reduction in color and toxicity of the effluent.

3. PROCESS DESIGN

The performance of oxidation ponds is affected by the prevailing environmental conditions such as air and waste temperature, wind velocity, solar radiation, and types of micro-organisms responsible for waste stabilization. The proper design for ponds must therefore involve the use of established design equations supplemented with results from laboratory model investigations simulating the local climate conditions as well as the shape of the treatment pond and the hydraulic flow patterns.

Thirumurthi ¹²⁷³ suggests that the design of oxidation ponds should be based on the Wehner-Wilke equation, which is derived for a chemical reactor with first order kinetics and a diffusivity constant:

$$\frac{S_e}{S_a} = \frac{4aL^{1/2}d}{(1+a)^2 L^{a/2}d - (1-a)^2 L^{-a/2}d} \quad (1)$$

where

$$a = \sqrt{1 + 4 Ktd}$$

$$d = \frac{D}{UL} = \frac{Dt}{L^2}$$

in which d is the dimensionless dispersion number or diffusivity constant, D is the axial dispersion coefficient in ft^2/hr , U is the fluid velocity in ft/hr , L is the characteristic length of travel path of a typical particle in the tank in ft , K is the first order BOD removal coefficient in day^{-1} , and t is the detention time in day.

The dispersion number d incorporates the hydraulic mixing characteristics of the system and has to be either evaluated experimentally or obtained from previous studies under identical conditions. For most oxidation ponds, the value of d seldom exceeds 1.0 and typically ranges from 0.1 to 0.3. For the two extreme cases of plug flow and complete mixing systems, the values of d are zero and infinity respectively.

The BOD removal coefficient k takes into account the organic loading, the influent waste qualities and other biological factors, and is the other parameter that has to be obtained from laboratory studies. The effect of temperature can be corrected by the correlation:

$$K_T = K_{20} 1.072^{T-20} \quad (2)$$

where K_T is the BOD removal coefficient at temperature T (C).

For oxidation ponds with dispersion number d less than one, the design equation (1) can be simplified by neglecting the second term in the denominator to:

$$\frac{S_e}{S_a} = \frac{4a e^{(1-a)/2d}}{(1+a)^2} \quad (3)$$

The use of equation (1) can also be simplified with the help of Figure 1, which was prepared by Thirumurthi for commonly expected BOD removal efficiencies and the corresponding values of K and d.

The design equation presented here predicts that long rectangular ponds, because of the lower dispersion number caused by the longer length of travel path, will have a higher efficiency of BOD removal. However, excessively long lengths are impractical because of maintenance problems and lack of suitable land space.

In designing an oxidation pond, the procedure is to first obtain values for the parameters K and d and then determine the detention period t from either Figure 1 or equation (3) for the specified BOD removal efficiency. The volume of the basin is then readily computed knowing the waste water flow rate.

A minimum of 2 ft and maximum of 6 ft liquid depth is recommended for oxidation ponds. Minimum depths are necessary to discourage weed growth, whereas deep ponds do not permit aerobic conditions.

The actual organic loading for the oxidation pond can be obtained from the waste water flow rate and influent BOD and the calculated basin volume. Current design standards for oxidation ponds normally specify an organic loading range from 20 to 100 lb BOD₅ per acre per day for handling raw wastes and 10 lb BOD per acre per day for polishing waste effluents from other treatment units. The medium organic loading values in lb BOD per acre per day for industries employing extensive use of oxidation ponds are: meat and poultry, 72; petroleum, 18; dairy, 22.

Detention times in oxidation ponds treating industrial wastes show extreme variations ranging from 1 day up to 90 days. The average retention time is approximately 30 days.

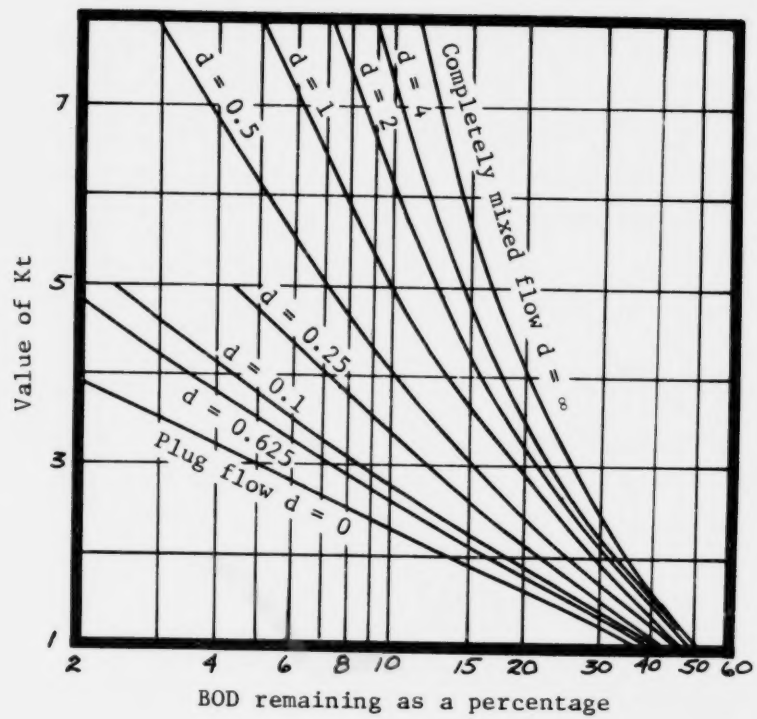


Figure 1. Oxidation Pond Design Formula Chart.

4. PROCESS ECONOMICS

The capital investment costs of oxidation ponds are relatively low, and range from \$20,000 for a one acre pond to about \$280,000 for a 30 acre pond,⁰⁵³⁴ when land values are not included. Approximate land requirements for oxidation ponds are 3-21 acres/MGD* of waste water flow.

Operating costs for oxidation ponds are determined by the waste water pumping and manpower costs, and are usually negligible contributions in a multistage waste treatment facility. Annual operating costs are of the order of 1,000 including analytical control.

5. PROCESS MODIFICATIONS

Oxidation ponds are simply shallow basins or lagoons where waste stabilization occurs under aerobic conditions when properly operated. Physical shapes of the ponds are usually either rectangular or square, but may also be dictated by the shape of the land available.

6. PROCESS APPLICABILITY

Oxidation ponds have been widely used in treating industrial waste waters when a high degree of purification is not required. In a 1962 survey¹²⁷² it was reported that more than 827 industrial premises in the United States employed oxidation ponds in waste treatment. Amongst those receiving treatment are wastes from meat and poultry packing stations, canneries, dairies, chemical plants, oil refineries and petrochemical works, paper and pulp mills, and textile mills. The typical BOD removal efficiencies reported were from 60 to 90 percent.

Since temperature changes have significant effects on algal activity and the effluent quality, designs of oxidation ponds should be based on the average temperature during the winter months.

* MGD = million gallons per day

More recently, oxidation ponds have proven to be quite successful in treating steel mill wastes.¹⁴²⁶ The Granite City Steel Company uses a 2-cell lagoon covering about 350 acres in an area fashioned out from an adjacent lake for treating a total of approximately 38 MGD of waste water. The pond system has a total capacity of 634 million gal. Detention times in the oxidation ponds are about 10 days for waste water from the blast furnace (for chemical contamination to disappear) and about 3-1/2 days for waste water from the rest of the steel plant. The reductions in various kinds of pollutants from the steel plant waste water by the oxidation pond system varies (Table 1) but generally indicates that the water quality discharged from the ponds is better in nearly every characteristic than that being withdrawn from the Mississippi River for the cooling and cleaning needs of the plant. The significant reductions in phenol and cyanide concentrations are particularly notable.

At a National Disposal Site for treating hazardous wastes, it is recommended that oxidation ponds be considered for installation as a polishing stage for effluents from other biological waste treatment processes. Because of the complexity and possible toxicity of the incinerator scrubber waste liquors, spent cleaning solution wastes and spill control system wastes which possibly will be handled at a National Disposal Site, a multistage biological treatment system involving trickling filter - activated sludge - oxidation ponds will probably be required on effluent water streams. Such biological treatment would follow the removal of toxic inorganic components from the streams.

TABLE 1
OXIDATION POND INFLUENT AND EFFLUENT
QUALITY AT GRANITE CITY STEEL PLANT

Oxidation Pond Influent and Effluent	Settleable Solids mg/l	Suspended Solids mg/l	COD ppm	BOD ppm	Grease ppm	NH ₃ ppm	Phenol ppb	Cyanides ppb	pH
Water Withdrawn from Mississippi River	0.60	62	24		3	1	10	5	7.84
Steelworks Effluent	0.10	41	68	8	-	0.4	12	4	7.10
Blast Furnace Effluent	0.10	98	93	10	-	14	1300	1800	7.58
Oxidation Pond Effluent	0.07	18	50	5	4	3	5	2	8.01

NOMENCLATURE

- d = dispersion number or diffusivity coefficient
- D = axial dispersion coefficient, ft^2/hr
- K = first order BOD removal coefficient, day^{-1}
- L = characteristic length of travel path of a typical particle in the pond, ft
- S_a = influent BOD, mg/l
- S_e = effluent BOD, mg/l
- T = temperature, $^{\circ}\text{C}$
- t = detention time, day
- U = fluid velocity, ft/hr

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TRICKLING FILTERS

1. INTRODUCTION

The trickling filter consists essentially of a rectangular or circular bed of rocks or synthetic media, usually from 3 to 15 ft deep, over which waste water is distributed. The medium serves as a habitat for bacteria growth, and organic material present in the waste is removed by the biological slime as the waste water flows through the filter. Proper hydraulic loading is maintained by recirculation of a portion of the filtered effluent.

Because of the short residence time, BOD removal by trickling filters is usually far from complete. For the same reason, however, toxic substances discharged into the system are less likely to cause complete disruption, and shock loadings have a less pronounced effect.

Trickling filters for industrial wastes are primarily used to level out and reduce organic loads in a multistage biological treatment system. A schematic flow diagram of a typical trickling filter system is provided (Figure 1).

2. OPERATION PRINCIPLE

The trickling filter process utilizes bacterial growths adhered to the bed packing for the biochemical oxidation of organic matter present in the waste water. A portion of the remaining organic material, however, is converted to new cells after being absorbed through a thin film into the biological slime on the surface of the filter medium. With the high rate type filter used for the treatment of industrial wastes, the hydraulic loading is such that a part of the attached growth is continuously sloughed off from the filter and a bacterial population equilibrium is often automatically maintained. The operation of the trickling filters is thus

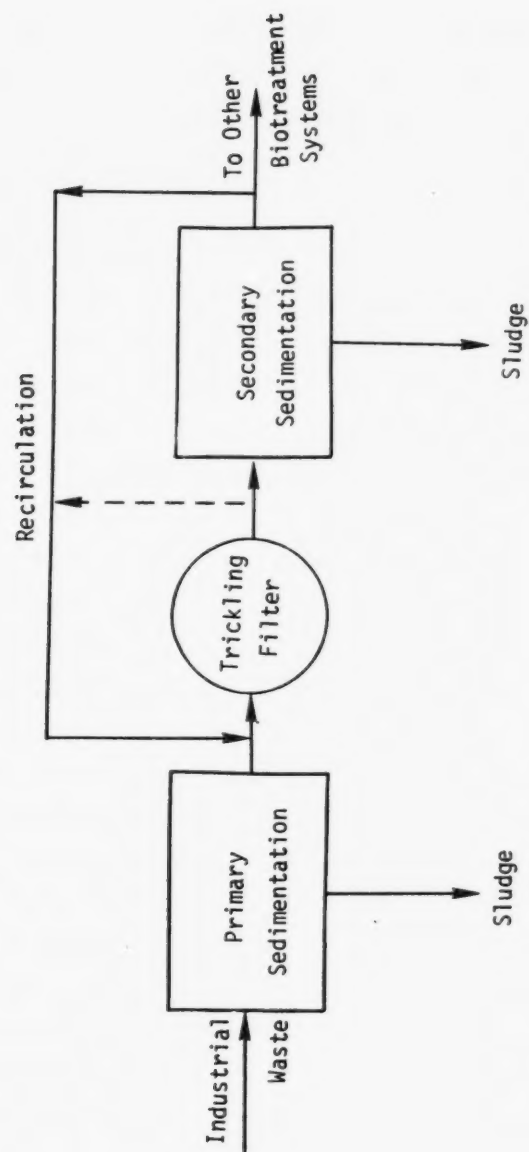


Figure 1. Trickling Filter Flow Diagram

very similar to that of the packed tower in chemical engineering unit operations, especially because different degrees of waste purification are obtained at different levels within the filter bed.

Proper functioning of trickling filters requires aerobic conditions in the bed and sufficient void space in the packing must be provided. Under normal conditions in properly designed filters, adequate air flow is usually produced by the temperature difference between the air and waste water.

3. PROCESS DESIGN

Trickling filters are generally 3 to 15 ft in depth and consist of a filter media retained by a wall over which waste water is evenly applied by either rotary distribution arms or fixed spray nozzles. An underdrain system is used to remove effluent from the filter and to provide air passage for the maintenance of aerobic conditions.

The filter medium provides surfaces for biological slime growth. The material constituting the medium should be hard, free from dust, resistant to the action of the waste treated, and a high surface area/volume ratio. The filter should have sufficient void space to permit air circulation.

For the treatment of industrial waste, rock and synthetic plastic have generally been used as the filter material. The synthetic media usually consist of flat or corrugated sheets or rigid materials assembled in units resembling a honeycomb, and are primarily used to treat wastes with higher hydraulic and organic loadings. Because of the controlled uniformity and void space, and a greater surface area/volume ratio, the plastic filter media provide greater BOD removal efficiency and are free from plugging and ventilation problems. The lightness of the plastic media also enables stacking to a greater height and trickling filter designs of depth up to 40 ft.

Trickling filters are normally designed according to the applied hydraulic and organic loadings. The hydraulic load is the total volume of waste water applied to the filter per day per unit area of surface area, and ranges from 25 to 100 gpd/ft² for high rate filters. The organic load is the pounds of 5 day BOD applied to the filter per day per unit volume of filter medium, and ranges from 5 to 25 lb BOD/day/1000 ft³ for standard rate filters and 25 to 300 lb BOD/day/1000 ft³ for high rate filters.

Recirculation is often utilized for high rate trickling filters to increase the filter efficiency and to dilute the initial high organic concentration in the waste. Recycle ratios as high as 40 are sometimes required.

The design of the trickling filter depends on the following variables: hydraulic rate of flow, filter depth, recirculation ratio, influent and specified effluent BOD, and also waste water temperature. Eckenfelder¹²⁷⁶ suggests the following formula for the removal of BOD from industrial wastes:

$$\frac{L_e}{L_o} = \frac{1}{1 + \frac{2.5 D^{0.67}}{\left(\frac{Q}{A}\right)^{0.5}}} \quad (1)$$

where L_e is the BOD of filter effluent in mg/l

L_o is the BOD actually applied to the filter (including recirculation) in mg/l

D is the depth of filter media in feet

Q is the plant influent rate in MGD

A is the filter surface area in acres

Eckenfelder also states that the effect of recirculation is to dilute the influent BOD (not including recirculation), L_i , by the formula:

$$L_o = \frac{L_i + R L_e}{1 + R} \quad (2)$$

where R is the recirculation ratio

The effect of waste water temperature is taken into account by Eckenfelder as:

$$E_T = E_{20} 1.035^{T-20} \quad (3)$$

where E_T is the filter BOD removal efficiency at temperature T (C) and E_{20} is the efficiency at 20 C.

The volume of the filter media is responsible for the major portion of the construction cost of the trickling filter systems. Using equations (1) and (2), the volume V in units of 1000 ft³ is:

$$V = 7.0 \frac{Q}{D^{0.33}} \frac{1}{(1 + R)^2} \left(\frac{E}{1 - E} \right)^2 \quad (4)$$

It is seen from the Eckenfelder formula that the filter media volume varies directly with the flow rate Q , is a function of efficiency as $E^2/(1-E)^2$ (influent BOD is not directly included as a parameter) and depth as $1/D^{0.33}$. It is also a function of recirculation as $1/(1 + R)^2$, which causes the volume to decrease with greater recirculation ratios. For practical purposes, however, further decrease in volume should not be considered in the design at recycle ratios about 4 or 5. Furthermore, designing for minimum filter medium volume by increasing bed depth and recirculation would also significantly increase the associated cost of pumping. The use of the Eckenfelder formulas described here for trickling filter process design usually gives better predicted values in filter performance than other design formulas.¹²⁷⁰

4. PROCESS ECONOMICS

The primary factors determining the capital cost of trickling filter systems include the waste flow rate and the organic loading. Depending on the treatment capacity (volume of the filter media), construction costs for trickling filters usually range from \$0.2 MM to \$3 MM.

Operating costs for trickling filter systems are normally due to pumping and distribution of waste water. For the treatment of chemical wastes, operating costs have ranged from \$700 to \$2000 per MG waste or \$50 to \$4000 per 1000 lb DO₂ removed.

5. PROCESS MODIFICATIONS

Modifications of the trickling filter systems generally involve differences in recirculation or distribution schemes,¹²⁶⁶ and are described very briefly here:

Biofilter

The biofilter utilizes a shallow trickling filter with recirculation and high rate of application. As indicated in the flow scheme (Figure 1), the effluent from either the filter or secondary sedimentation is recirculated back to the primary sedimentation tank.

Accelofilter

In the accelofilter system (Figure 2), a portion of the filter effluent is directly recirculated back to the trickling filter, and places no additional burden on the sedimentation tanks.

Aerofilter

In the aerofilter system (Figure 3), a portion of the effluent from secondary sedimentation is recirculated back to the filter, where the waste is applied continuously by high speed disc distributors. Normal hydraulic loadings are greater than 300 gpd/ft² of surface area.

6. PROCESS APPLICABILITY

Trickling filters have been extensively used in the treatment of industrial wastes due to their ability to cope with shock loading by maintaining proper hydraulic loading with recirculation. Industrial wastes that have been successfully handled by the process include the following: acetaldehyde, acetic acid, acetone, acrolein, alcohols, benzene, butadiene, chlorinated hydrocarbons, cyanides, epichlorohydrin, formaldehyde, formic acid, ketones, monoethanolamine, phenolics, propylene dichloride, terpenes, ammonia, ammonium nitrate, nylon and nylon chemical intermediates, resins, and rocket fuels. A summary of the types of petrochemical and organic wastes treated by the trickling filter process along with the effluent qualities obtained, has been presented by Jones (Table 1). The BOD removal efficiencies range from a low of 30 percent to a high of 98 percent.

In general, the materials that are toxic to the bacteria in the activated sludge have the same effects on the biological slimes in the trickling filter. The maximum limits for selected waste water characteristics could be obtained from Table 2 of the Activated Sludge Process Evaluation.

Below threshold toxic limits of the bacteria, metal content in the waste water could be reduced by the trickling filter process. The approximate amounts removed by the process are: Cr, 30 percent; Ni, 40 percent; Zn, 30 percent; Pb, 30 percent; Cu, 20 percent,⁰⁶⁶⁹. These metals are concentrated in the biological sludges obtained from the secondary sedimentation tank which must be disposed of later.

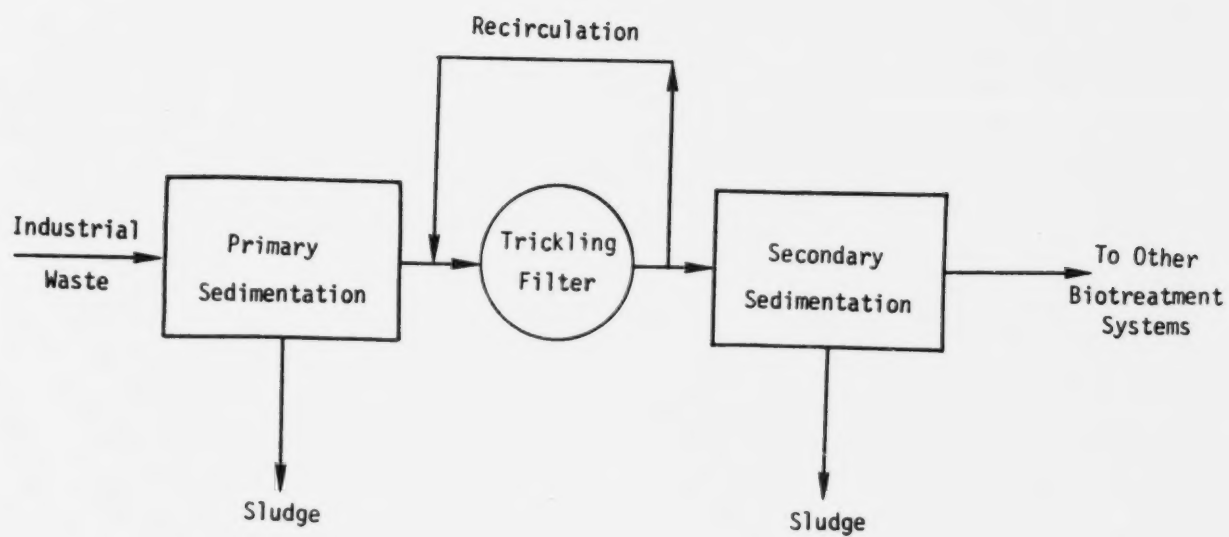


Figure 2. Accelofilter

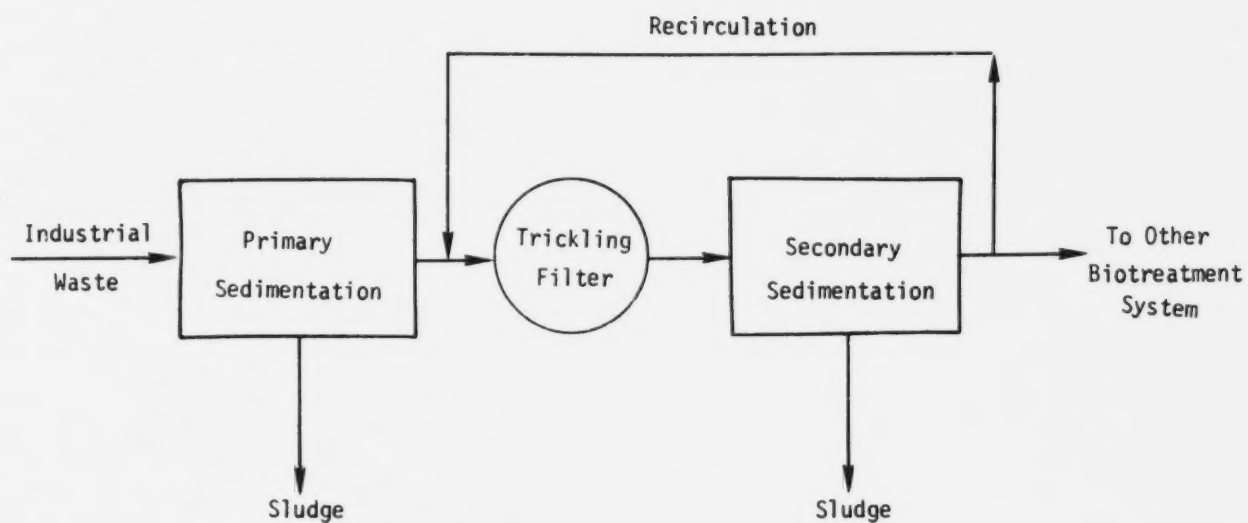


Figure 3. Aerofilter

TABLE 1.
TRICKLING FILTER TREATMENT OF
INDUSTRIAL ORGANIC WASTES[†]

Product and/or Process	Flow (MGD)	BOD			COD			Organic Loading lb BOD ₅ /day (1,000 ft ³)	Deficient Nutrients	Remarks
		In (mg/l)	Out (mg/l)	Rem (%)	In (mg/l)	Out (mg/l)	Rem (%)			
Phenol, Salicylic Acid, Rubber Chem., Aspirin, Phenacetin, Phthalic Anhydride	2.59	190	58	69.5				40.5	None	Rock Media, recirc. ratio 2.84:1
	2.59	58	34	41.5				11.8	None	Rock Media, treats effluent from above filter, effluent to act. sludge
Plastics, Amines, Enzymes	1.06	1,960	37	98.1	2,660	230	91.5			2 filters, followed
Ethylene, Propylene, Butadiene, Benzene, Polyethylene, Fuel Oil	0.63	170	85	50	400	200	50	89	None	Plastic filter media followed by act. sludge phenol removal = 95% influent diluted 2:1 w/cooling water
Aliphatic Acids, Esters, Alcohols, Aromatic, Amines, Inorganic Salts	0.57-0.86	1,100-2,300	23-470	57-99				42.1-82 (Both filters combined)	None	pH adjusted prior to treatment; 2 filters in series; Recycle on 1st stage is 14-21:1
Ethylene, Propylene, Butadiene, Benzene, Naphthalene, Phenol, Acrylonitrile, Soft. Detergent Bases, Resins	0.43	1,300			1,500	450	60-70	140	NH ₃ , PO ₄	Sour Waters, Rock Media
Pentaerythritol Waste contains Formaldehyde, Sodium Formate, Methanol, Pentaerythritol	0.118	5,080-5,800	225-232*	95-96*				1st stage 65	NH ₃ , PO ₄ , Yes	2 filters in series followed by act. sludge; recycle 40:1 on prim. filter, 13:1 second
Resins-Formam, Aminoplasts, Phenol-Formal, Epoxy Resins, Textile Aux.	0.17			82.6				11.7	None	Both filters treat act. sludge effluent, Blast furnace slag media
	0.03			89.3				14.6	None	Waste contains phenol, formaldehyde, methanol
Acrylic Fibers	0.32		13	30-70	49	30-70		50-84	NH ₃ , PO ₄	Waste contains: acrylonitrile and zinc plastic filter media
Synthetic Resins-Phenol, Formaldehyde, Fatty acids, Phthalic Acid, Maleic Acid, Glycerol, Pentaerythritol, H.C. Solvents				95-98				1st stage 85 (as Phenol) 2nd stage 11.6-18.2 gpd/ft ³		Plastic media, 2-stage treatment; Influent: Phenol = 4,500 mg/l Formaldehyde = 2,000 mg/l Fatty acids = 800 mg/l Phthalic and maleic acids = 1,000 mg/l Eff. phenol = 1.5 mg/l
Waste contains Acrylates, Acetone, Inhibitor oils, Alcohols, Esters, H ₂ SO ₄ , Organic Acids								51-79	None	Original loading was lower value, loading increased w/o any adverse effects 15,000 lb BOD ₅ removal per day

* Entire treatment system

† Table 41⁰⁵³⁴

The complexity of industrial organic wastes and the stringent specification of effluent qualities have at times circumvented the use of trickling systems as a single stage treatment unit. At a National Disposal Site for the disposal of hazardous wastes, it is recommended that trickling filters be installed as a roughing device and the first stage in a multistage biological treatment facility. For example, systems can be designed with high rate trickling filters in series with the activated sludge process, to take advantage of the trickling filter's ability to handle shock loads and the ability of the activated sludge process to produce an effluent of high quality, and thus eliminate some of the shortcomings of each.

One distinct disadvantage of the installation of trickling filters at National Disposal Sites is their unsuitability for treating waste waters that are discharged intermittently or infrequently as might be the cases with the effluents from batch operations. Under these conditions, the filters would not function efficiently as they are designed to run continuously. A possible solution to this problem is the parallel use of trickling filters and aerated lagoons as the first stage in a multistage biological treatment unit, so that occasional overflows and irregular discharges could be directed to the lagoons, which also serve as equilization tanks for the second stage biological treatment process.

NOMENCLATURE

- A = filter surface area, acres
- D = depth of filter media, ft
- E_T = filter BOD removal efficiency at T C
- L_e = BOD of filter effluent, mg/l
- L_i = BOD of filter influent (not including recirculation), mg/l
- L_o = BOD actually applied to filter (including recirculation), mg/l
- Q = rate of waste water flow, MGD
- R = recirculation ratio
- T = temperature, C
- V = volume of the filter media, 1000 ft³

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HAZARDOUS WASTE DISPOSAL PROCESS DESCRIPTOR-DIALYSIS

1. INTRODUCTION

Dialysis is a process by which various substances in solution having widely different molecular weights may be separated by solute diffusion through semi-permeable membranes.¹⁴⁵² The driving force is the difference in chemical activity of the transferred species on the two sides of the membrane. Until recently, dialysis was of limited applicability because the parchment membranes used had very poor acid resistance, but the development of microporous polyvinyl chloride membranes has extended its range of application from the recovery of caustic soda in viscose rayon production to the recovery of mineral acids from aqueous solutions and the recovery of colloidal organics in the manufacture of pharmaceuticals.¹⁴⁵³

The process is basically passive with feed solution moving into a two-dimensional cellular array and then separating into waste and product streams, and is used for caustic recovery from a caustic-hemicellulose feed in the rayon industry (Figure 1)¹⁴⁵⁴

2. OPERATING PRINCIPLES

Dialysis may be described in terms of a diffusion process. For steady-state mass transfer through a membrane with countercurrent flow of the solutions,¹⁴⁵²

$$W = V_o A \Delta C_{lm} \quad (1)$$

where W = mass transferred in g/min, V_o = overall dialysis coefficient in cm/min, A = membrane area in cm^2 , and ΔC_{lm} = logarithmic mean concentration gradient across the membrane, i.e.,

$$\frac{\Delta C_1 - \Delta C_2}{\ln(\Delta C_1 / \Delta C_2)}$$

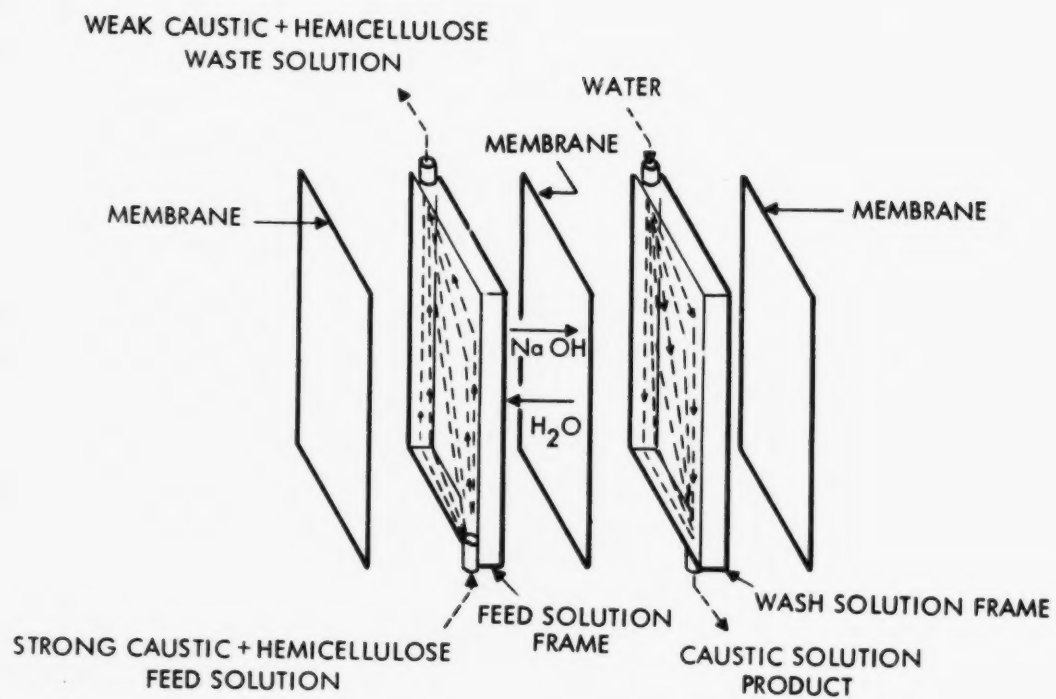


Figure 1. Plate-and-Frame Dialyzer 1454

where ΔC_1 and ΔC_2 are the respective inlet and outlet concentration differences in g/cc.

This relationship is only approximately correct,¹⁴³³ although reasonably accurate estimates can be made by adjustment of the coefficient V_0 . Complications are introduced by the two-dimensional nature of the concentration gradient; not only is there a gradient in the direction of diffusion through the membrane, but there is also a gradient in the direction parallel to the membrane as the feed solution is progressively depleted of solute in its traverse from one corner of the cell to the other. The passage of solvent through the membrane, particularly when concentrated solutions are involved, decreases the efficiency of the process and entails a modification of Eq. 1 to reduce the area A to an effective A' .^{1452,1454}

As dialysis has gained wider attention and investigative interest, the simple concept of a porous membrane which admits or rejects species on the basis of their molecular dimensions has given way to complex, poorly understood ideas involving membrane-species interactions, electrostatic effects, and microelastic effects in the neighborhoods of the individual pores. The science is still relatively primitive, but these principles have been utilized in the recent art.

3. PROCESS DESIGN

As with reverse osmosis, the characteristics of the dialysis membrane are the determining factors in the application of dialysis to any particular operation. The membrane must of course be chemically resistant to the materials in the feed stream. Parchment has long been used successfully for neutral and basic streams, and new polyvinyl chloride membranes have been used successfully for acid streams.

The chemical and physical properties desired for a dialysis membrane material are summarized succinctly by Kirk-Othmer:¹⁴³³

"Selection of the membrane polymer is a key factor in determining diffusion properties. Ability to swell in the dialysis solvent is important if high rate and low selectivity among

small molecules are sought, since swelling generally increases greatly the mobilities of the diffusing species. Solubility and chemical behavior in the dialysis solvent of the units of the polymer chain are strong factors affecting swelling. For the selective, rapid transport of a particular species, the membrane units should be chosen to be good and unique solvents for that species. All practical membranes must not only possess good diffusional properties but must also remain insoluble in the dialysis media, and must maintain sufficient mechanical strength to withstand handling and momentary or sustained pressure differences, depending on the process. The compromise between strength and diffusional properties may be achieved in many ways. Membranes may be cast on a fabric of open weave, or thin, strong fibers may be combined with the casting solution. Strength compromises may be achieved in homogeneous membranes by the use of polymer mixtures, copolymers of the random or alternating type, or the less familiar block copolymers (Figure 2). The latter system is made up of polymer chains comprised of two monomer units with each monomer unit attached to its own type many times.

Membranes developed to date generally have a maximum operating temperature of 120 F.¹⁴⁵³

To maximize the amount of material transferred in a unit, the overall dialysis coefficient, V_0 must be as large as possible. For purposes of analysis, V_0 may be conveniently broken down into two terms,^{1433,1452}

$$\frac{1}{V_0} = \frac{1}{V_1} + \frac{1}{V_2} \quad (2)$$

where V_1 = dialysis coefficient in the liquid film adjacent to the membrane and is approximately equal to 1000 times the normal diffusion coefficient for the species in the solvent medium, and V_2 = membrane dialysis coefficient, which may be approximated by the expression $\frac{60D}{h^2} \frac{FV'}{h^2}$ where D is the

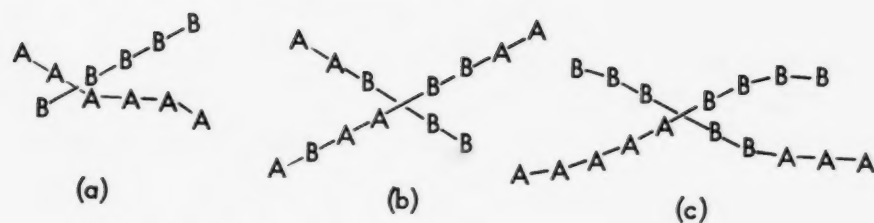


Figure 2. (a) Mixture of two homopolymers. (b) Random copolymer. (c) Block copolymer.

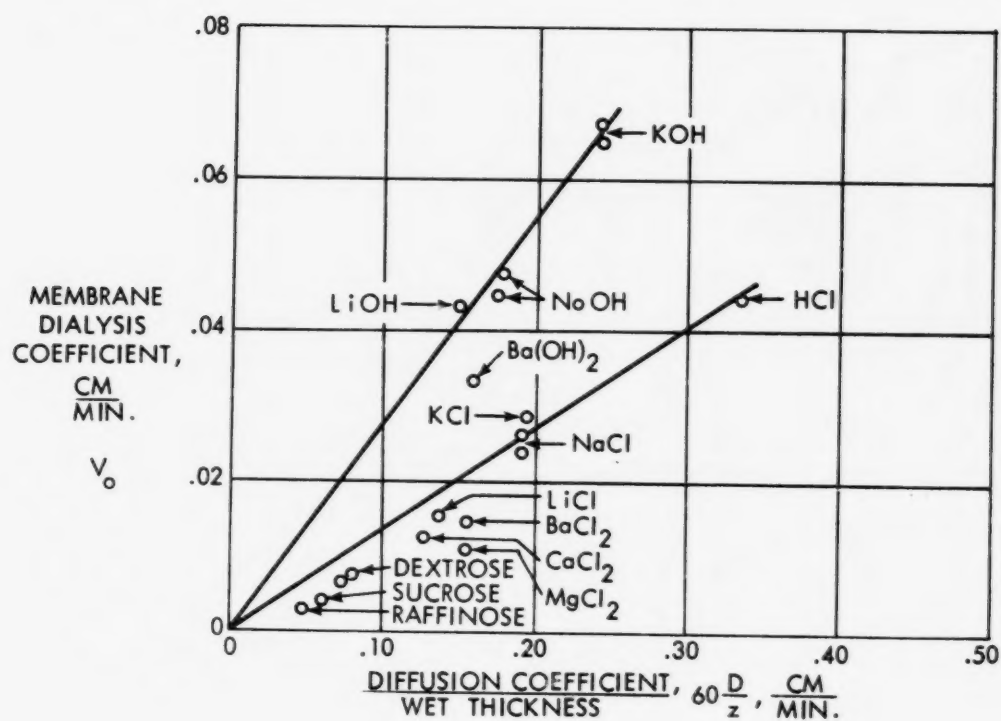


Figure 3. Experimental Membrane Dialysis Rates 1454

diffusion coefficient, F is a drag factor which accounts for the interference of the membrane with the normal diffusive flow, V' is the volume fraction of the membrane occupied by pores, h is the tortuosity (ratio of capillary length to membrane wet thickness), and Z is the membrane wet thickness. Perry¹⁴⁵² presents values for these parameters for a variety of commercially available membranes. These will not be pursued further here except to note that they are largely experimentally derived and attempts have been made¹⁴⁵⁴ to predict V_0 from a minimum number of parameters with fair success. Figure 3¹⁴⁵⁴ presents experimentally-determined values for V_0 for a variety of bases, salts, and sugars for a typical dialysis membrane, viz., DuPont 450 P.D. cellophane. Table 1¹⁴⁵³ presents diffusion coefficients for several common acids, bases, and salts. It should be noted that widely separate coefficients, e.g., H_2SO_4 vs $CuSO_4$, imply disparate values of V_0 and the possibility of efficient separation by dialysis.

This analysis indicates that, for maximum material transfer, the inter-membrane spacing and membrane thickness are both minimized, so that, with considerations of surface area and concentration gradients as presented in Eq. 1, the ideal dialysis unit has a flow path of great width, small inter-membrane spacing and membrane thickness, and short length. However, practical design considerations work against these extremes, with the result that stream convection velocities parallel to the membranes may be as low as 0.1 cm/min.

The required membrane area for a given throughput and recovery is increased as a function of the solute concentration in the feed stream and the ration of D_{H_2O}/D_{solute} . Figure 4¹⁴⁵² presents a series of parametric curves showing the approximate corrections required.

Several limitations of variable severity are encountered in the design of any dialysis plant. Since dialysis is essentially a passive process which draws on no outside energy source, separations can be painfully slow and required area-to-volume ratios may prove difficult to achieve technically and difficult to justify economically. Furthermore, if the chemical potentials of the diffusing species on either side of the membrane do not remain

TABLE 1

REPRESENTATIVE DIFFUSION COEFFICIENTS¹⁴⁵³ACIDS

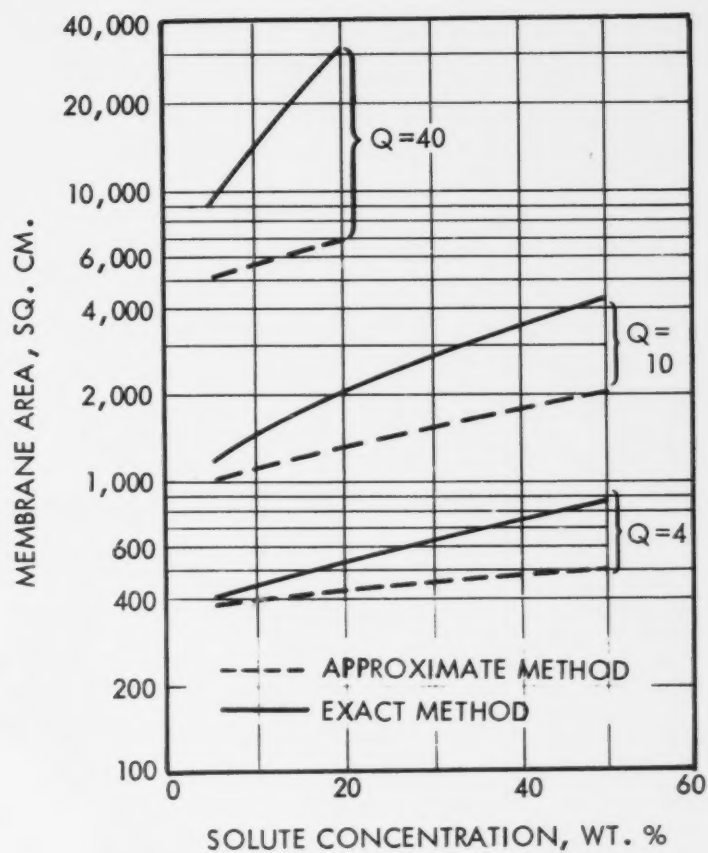
Hydrochloric	2.6
Nitric	2.6
Sulfuric	1.7
Acetic	0.88
Phosphoric	0.9

ALKALIES

Sodium Hydroxide	1.5
Potassium Hydroxide	2.3

SALTS

Sodium Chloride	0.35
Sodium Sulfate	0.77
Copper Sulfate	0.58
Zinc Sulfate	0.59
Nickel Chloride	1.1



$$Q = \frac{\text{DIFFUSION COEFFICIENT OF WATER}}{\text{DIFFUSION COEFFICIENT OF SOLUTE}}$$

Figure 4. Calculated membrane area to recover 90% of solute at a feed rate of 100 g/min. 1452

disparate, the driving force for separation will be severely reduced. This happens when there is a low initial concentration in the feed stream or a required low final concentration in the waste or product stream. Low is generally under 0.1 percent. (Figure 5¹⁴⁵² relates the required membrane area, dialysis coefficient, and feed stream flowrate to the desired recovery for a series of feed stream/product stream ratios. For a desired recovery of 75 percent and a feed stream/product stream ratio of 2/3, $AV_0/q = 2.3$, so that for $q = 10,000$ gpd and $V_0 = 0.04$ cm/min, $A = 706$ ft².

In addition, if the dialysis coefficients of two solutes are close together, the efficiency of their separation will be very poor. This occurs whenever molecular dimensions and molecular weights are close together. Figures 6 and 7¹⁴⁵⁴ are parametric representations of experimental results for attempted separations of a Na_2SO_4 -sucrose solution. Here both molecules are under 10 Å in diameter. Note that as the pore size decreases in the direction of the size of the smaller Na_2SO_4 molecule, the ratio

$$\frac{V_0(\text{Na}_2\text{SO}_4)}{V_0(\text{sucrose})}$$

increases, as does the separation efficiency. But, for a given pore size, however, good separation efficiency results in a lower total recovery of the Na_2SO_4 .

4. PROCESS ECONOMICS

It is difficult to arrive at valid cost estimates for large-scale dialysis systems because the problems of slow separation and large required surface-to-volume ratios have hitherto hindered large-scale commercial exploitation of dialysis. It is to be expected that capital investment would be high for these reasons, but that operating requirements would be low, since no energy input is required save for low pumping speed. Dvorin¹⁴⁵³ is optimistic that the newer membranes will prove to be essentially maintenance-free, but no actual field data was found. Perry¹⁴⁵² reports a selection of dialysis units available in 1960. These are continuous counter-current units, consisting of a series of alternate water and solution cells

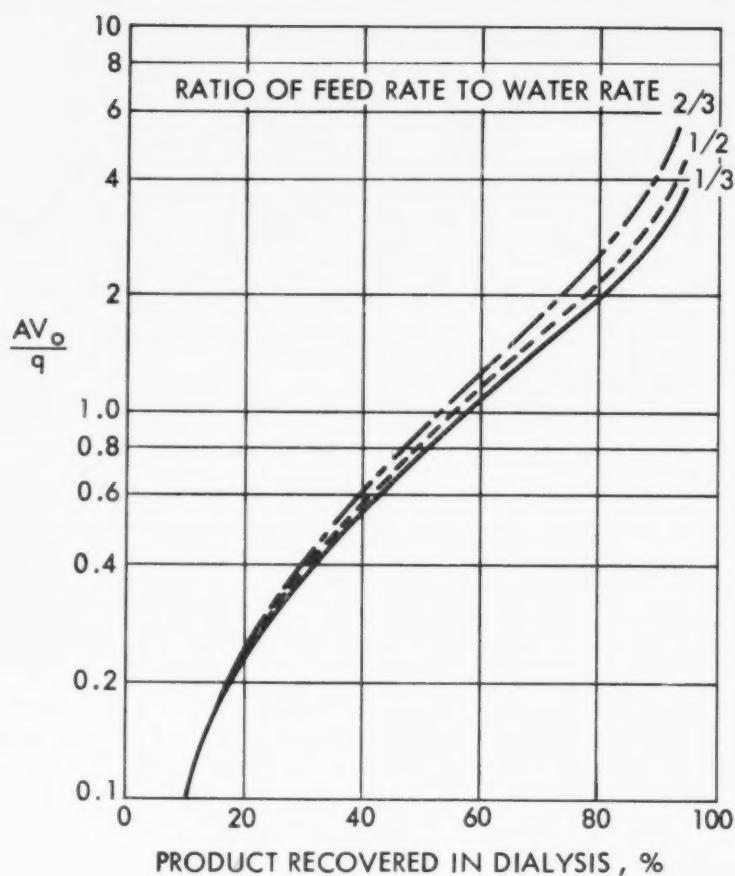


Figure 5. Membrane area required vs product recovery at various values of feed-to-water flow rates; A = area sq. cm; U_o = overall dialysis coefficient, cm/min; q = flow rate of feed solution, cu. cm/min. ¹⁴⁵²

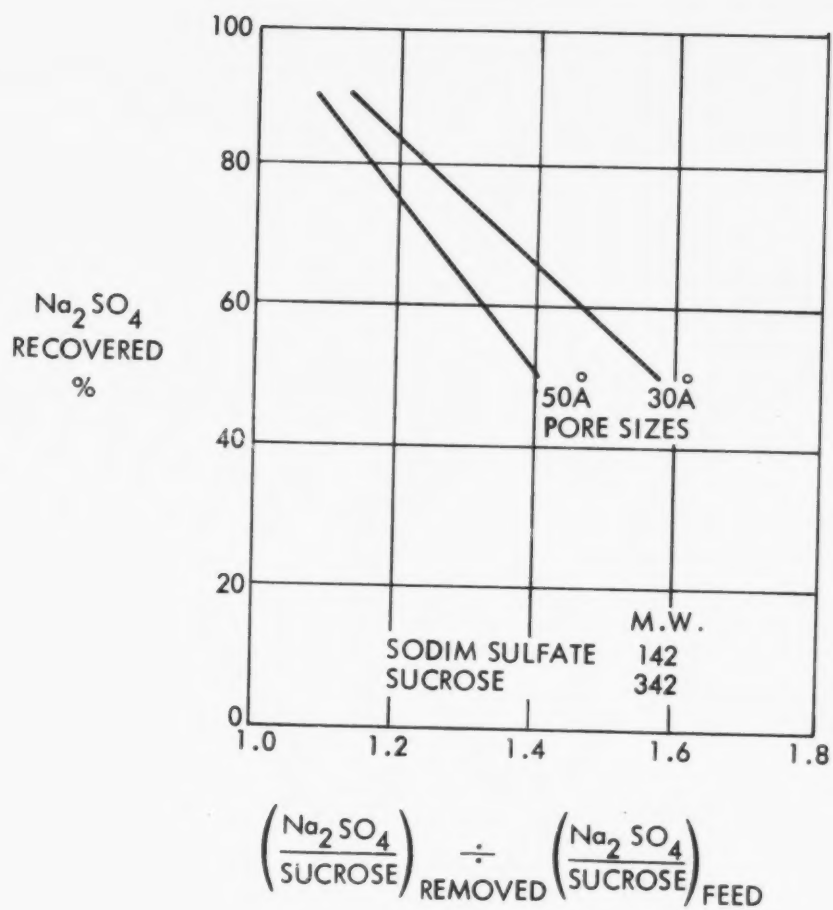


Figure 6. Dialytic Fractionation 1454

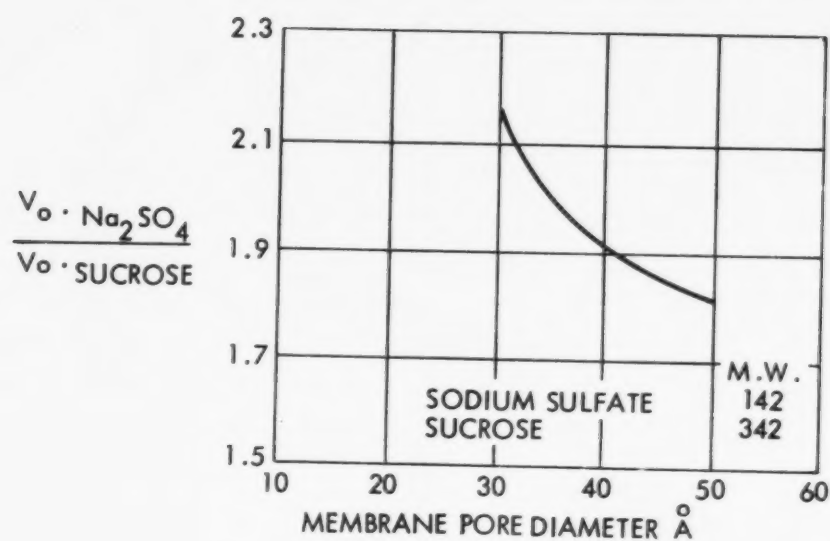


Figure 7. Dialysis Rate vs Pore Diameter 1454

connected in parallel and separated by the membranes. The Brosites Machine Company supplies a unit containing 850 ft² of membrane for \$10,900 + installation, and the Graver Water Conditioning Company, New York, supplies a unit containing 1,000 ft² of membrane for \$9,000 + installation. Laboratory-size units are also available.

5. PROCESS MODIFICATIONS

Process modifications are concerned primarily with attempts to increase the speed of separation and the concentration differences between the feed and product streams. Dialysis may be used in conjunction with energy-input processes. Various processes such as boiling and condensing in distillation, solvent processing in extraction, and chemical regeneration in ion exchange have been considered in attempts to increase energy differences in the respective streams and thereby speed the process. Concentration differences may be promoted by the recycling of the waste stream. Figure 8 shows a process flow sheet for an acid recovery unit incorporating recycling in a copper refinery.¹⁴³³

6. PROCESS APPLICABILITY

The unique characteristic of dialysis is its passivity and lack of reliance on any external energy input. This is of advantage when time is not a limiting factor or when it is desired to separate species in solutions of high concentration, e.g., 20 to 50 percent, where the energy requirements of other processes such as electrodialysis are very high.

The oldest continuing commercial use to dialysis is in the textile industry where feed streams containing 17 to 20 percent NaOH contaminated with hemicellulose are routinely recovered to 9 to 10 percent NaOH virtually free of the hemicellulose.¹⁴³³ An 800 ft² unit with 0.5 inch intermembrane spacing will typically handle 3600 gpd with a fluid residence time of 2 hr and a total caustic recovery of 200 tons/yr.

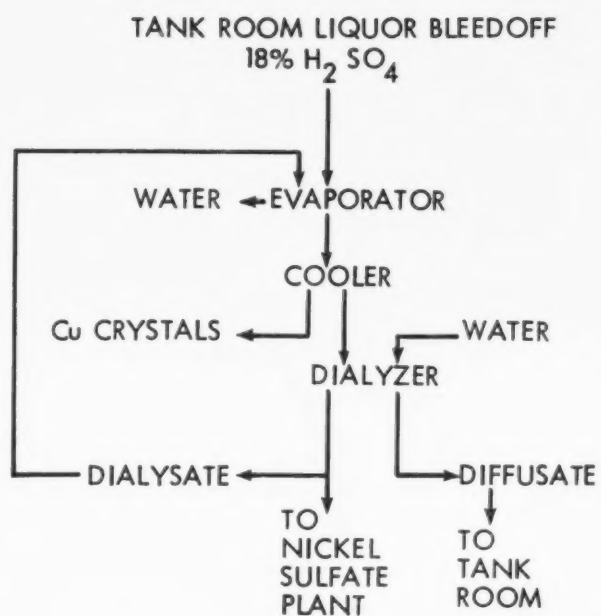


Figure 8. Process Flow sheet for acid recovery from salt solution with recycling 1433

Dialysis is particularly applicable when concentrations are high and dialysis coefficients are widely disparate (see Section 3 Process Design). Dvorin¹⁴⁵³ reports success in treating concentrated acid waste streams from metal finishing shops and refineries. Good recoveries are claimed for chromic, hydrochloric, nitric, hydrofluoric, and sulfuric acids. Results are quoted in Table 2 for an acid recovery unit in a copper refinery which produced essentially Ni-free H_2SO_4 . It is possible to improve efficiencies by recycling the waste stream. A representative process flow sheet incorporating recycling is provided (Figure 8).¹⁴³³

Dialysis is a suitable means of separation for any materials on the hazardous materials list which form aqueous solutions, e.g., inorganic salts such as ammonium chromate, or acids and bases such as phosphoric acid and sodium hydroxide. It is particularly suitable where high solute concentrations are involved, since reverse osmosis is then inapplicable and electro-dialysis requires large energy inputs and concomitant high cost. Its inherent passivity, however, makes it inefficient where concentrations of feed or product solutions are much below 0.1 percent. With regard to acids and bases, dialysis does not require neutralization prior to treatment, as reverse osmosis does. But no dialysis membranes presently available are suitable for both acids and bases.

With regard to National Disposal Sites, dialysis could most effectively be used for the further concentration of concentrated waste streams of extreme pH. The waste would then be stored or recycled to the supplier.

TABLE 2
RECOVERY RESULTS IN A COPPER REFINERY¹⁴⁵³

	Liquor Feed	Water Feed	Dialysate Effluent	Diffusate Effluent
Gal/Hr	400	400	420	380
H ₂ SO ₄ g/l	300	0	100	200
CuSO ₄ -Cu g/l	30	0	26	2
NiSO ₄ -Ni g/l	45	0	43	Trace

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HAZARDOUS WASTE PROCESS DESCRIPTOR--ELECTRODIALYSIS

1. INTRODUCTION

Electrodialysis is similar to dialysis in that dissolved solids are separated from their solvent by passage through a semi-permeable membrane. It differs from dialysis in its dependence on an electric field as the driving force for the separation. Thus the passivity and concomitant low energy requirements of the dialysis process are traded for the speed of separation associated with an energy-intensive process.

The membranes employed are specific for the passage of either cations or anions, and since the driving force is the electric field, only electrically-charged species can be separated. The process is shown schematically (Figure 1)¹⁶⁴⁵ for the desalination of brackish water, the most popular application to date.¹⁴⁵² As seen in the figure, the membranes are alternately cation-specific and anion-specific; so that, when the electric field is applied, the ions will segregate from the solvent to form a concentrated waste solution and fresh water. Sixty or more cells may be stacked in parallel and five or six stacks are often placed in series to achieve the 95 percent removal efficiencies obtained with reverse osmosis or dialysis.

2. OPERATING PRINCIPLES

Electrodialysis depends on the forced migration of ions selectively through a membrane. The driving force is an electric field set between two electrodes toward which the ions flow. The amount of material which can be processed is governed by the voltage and manifold pressure which can be applied without jeopardizing the structural integrity and materials properties of the membranes and the plumbing.

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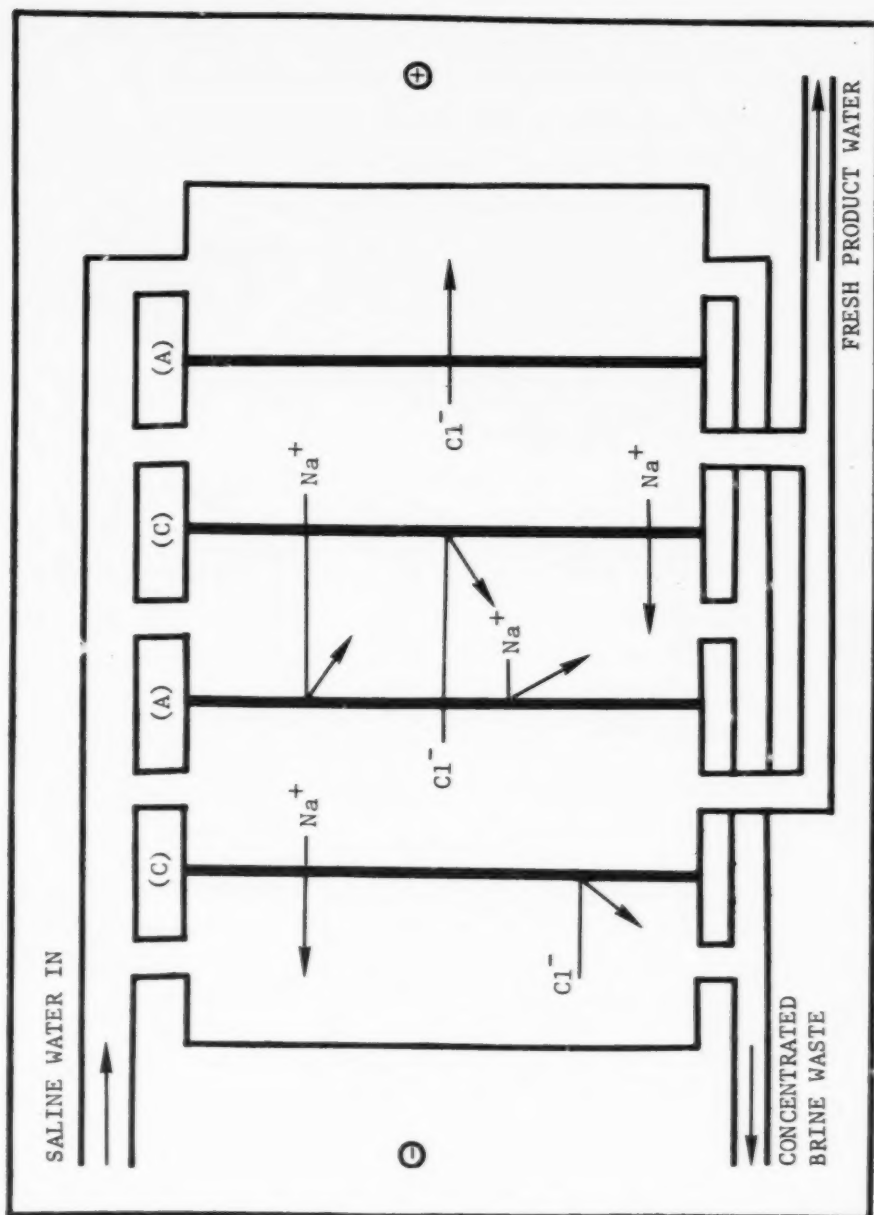


Figure 1. Electrodialysis Process

Electrodialysis membranes are insoluble polyelectrolytes, electrically-charged polymers, which ideally have high electrical conductivity and high selectivity for transport of the desired ionic species. Other desirable characteristics are mechanical strength, chemical stability, and resistance to fouling.^{1433,1452} A popular membrane consists of polystyrene made insoluble by cross-linking with divinyl benzene. The cation-permeable membrane is then made by sulfonating with sulfuric acid to 5 meq/g dry weight. Similarly, the anion-permeable membrane is made by chemically bonding quaternary ammonium groups to the polystyrene at a concentration of 1 to 3 meq/g dry weight. Unlike reverse osmosis or dialysis, there have been no significant innovations in electrodialysis in the past few years, so that the technology is assumed to be relatively mature.¹⁶⁴⁸

3. PROCESS DESIGN

It is advantageous to put as many cells as possible in series with the electrodes¹⁴³³ because: (1) the energy consumed at the electrodes is relatively constant with respect to the number of cells, (2) a pair of electrodes costs approximately ten times as much as a pair of membranes, and (3) membranes adjacent to the electrodes are subject to a more severe environment and degrade more easily. The total number of cells in a unit is limited by the maximum voltage which can be safely applied and general plumbing considerations.

Many theoretical and empirical expressions for the energy and power required for a given separation of a feed stream into a dilute product stream and a concentrated waste stream have been derived.^{1433,1653} A particularly useful one for design considerations is:

$$V = k \frac{F_P}{A} (N_f - N_d) \left(\log \frac{N_f}{N_d} \right) \left(\frac{R_{op} N_{av}}{E^2} \right) \quad (1)$$

where V = power consumption, kilowatt-hours per 1,000 gallons

F_p = total concentrated stream flowrate, gallons per hour

A = total cell-pair area, square feet

N_{av} = concentrated stream normality, equivalents per liter

N_f = feed stream normality, equivalents per liter

N_d = dilute stream normality, equivalents per liter

k = conversion factor = 25.4

R_{op} = resistance of 1 square centimeter of a cell pair (dilute solution + concentrated solution + cation - permeable membrane + anion - permeable membrane + polarized layers adjacent to membranes), ohm - square centimeters

$$E = \text{current efficiency} = \frac{F(N_f - N_d) f_d}{I n}$$

where

F = Faraday's constant, 96,500 coulombs per equivalent

f_d = dilute stream flowrate, liters per second

I = current, amperes

n = total number of cell pairs

Power requirements may run 10 kwh/1,000 gal. for 90 percent removal in an 880,000 gpd treatment plant with feedwater concentrations of 2000 ppm.^{1651,1652}

The resistances in equation 1 are usually empirically determined. They are not particularly amenable to design variation. When feedstream concentrations are 1000 ppm or more, current efficiencies may drop drastically with concomitant increases in power consumption. These decreases are usually attributable to decreases in membrane selectivity with increasing concentrations, back diffusion of the solute ions, diffusion of solvent through membranes, and electrical short circuiting through the solvent and the plumbing. Also, polarization of the membrane and its vicinity may become significant, and further decrease efficiencies and membrane life.

Back diffusion of the solute ions may be decreased by increasing the current density. This also decreases the capital cost of the electrodialysis plant, but increases the operating costs, since more power is required. Also, if the current density is too high, the membrane and the solution in its vicinity become polarized. Polarization is a serious and costly problem, because it leads to hydrolysis of the membrane and precipitation. The prospect of polarization inhibits wide variations in the operating parameters. Most electrodialysis units operate successfully with current densities in the range 0.05 - 0.08 amp/cm².

Electrical short circuiting is minimized by increasing the velocity in the system to decrease stagnation and associated charge build-up. This is most easily accomplished by restricting pipe diameters. The benefits must be traded against the increased pumping costs involved.

Leakage of solute ions through the wrong membrane is a function of concentration and ionic size and charge. For multivalent ions of large size it is almost nil, while hydrogen ions pass quite easily. The transport number which is defined as the ratio of ions which pass a plane with and without the membrane present, varies for various ions under several different conditions (Table 1).¹⁴⁵² A perfect membrane gives a transport number of zero for the wrong ion and a transport number of unity for the right one.

Operation is restricted to temperatures under 100 F to promote membrane life. Removal efficiencies increase markedly with temperature and number of stages* (Table 2).^{1651,1652}

With strong acid or base groups in the polyelectrolyte membrane, the membranes are relatively insensitive to pH and operation over a range of pH 1 to 14 is common¹⁴³³. If weak groups such as acetic acid are used, the membranes are sensitive to hydrolysis and the pH of the solutions must be kept within a narrow range. Therefore, strong groups are used almost exclusively.

*each stage consisting of 60+ cells

TABLE 1
SELECTIVITY OF IONIC-BARRIER MEMBRANES

Barrier	Solutions 1N		Permeable ion	Leakage ion	Transport No.* leakage ion
Anion	NaCl	NaOH	Na ⁺	OH ⁻	0.3100
	Na ₂ SO ₄	NaCl	Na ⁺	Cl ⁻	0.0500
	NaCl	Na ₂ SO ₄	Na ⁺	SO ₄ ⁻⁻	0.0030
	MgSO ₄	MgCl ₂	Mg ⁺⁺	Cl ⁻	0.1200
Cation	NaCl	HCl	Cl ⁻	H ⁺	0.5200
	HCl	NaCl	Cl ⁻	Na ⁺	0.0090
	NaCl	MgCl ₂	Cl ⁻	Mg ⁺⁺	0.0002

* Current density 90 amp./sq. ft.

TABLE 2
TYPICAL MINERAL REMOVALS FOR ED UNITS
AT DIFFERENT WATER TEMPERATURES

		Temperature		
		50 F	75 F	100° F
Two Stage	ED	51 - 65%	62 - 79%	76 - 88%
Four Stage	ED	76 - 88%	85 - 95%	94 - 98%
Six Stage	ED	88 - 96%	94 - 99%	98 - 99+%

Auxiliary equipment includes a manifold system to direct the respective feed, dilute, and concentrated streams into and out of the system and the assorted pumps, plumbing, valves, and instrumentation required in almost any chemical engineering operation. A source of DC power is of course required. This may run to 400 KVA for an 800,000 gpd plant.

4. PROCESS ECONOMICS

On a per stage basis, capital and operating costs for an electrodialysis plant are low. However, each stage has only a 35 to 45 percent per pass efficiency in removing dissolved solids,^{1452,1651,1652} so many stages may be required to obtain water of acceptable quality, with proportionate increases in cost. The Sanitation Districts of Los Angeles County^{1648,1649} have operated a 15,000 gpd electrodialysis pilot plant with the object of reducing the TDS of a secondary sewage treatment effluent. The results indicate that electrodialysis is not economically viable when compared to reverse osmosis, as shown by the projected capital and operating costs for a 10 million gpd system (Table 3). Note that the reduction in TDS was only 34 percent for this single stage unit and additional 34 percent stepwise reductions could only be obtained by increasing the number of stages with essentially no reductions in per stage costs.

A cost breakdown for a 28,000 gpd facility installed at Coalinga, California to make brackish water potable has been presented by Farrell and Smith (Table 4).¹⁶⁴⁷ No information with regard to concentrations is available.¹⁴³³ Parametric studies of cost as a function of required reduction in TDS and plant capacity have been performed (Figures 2 and 3).¹⁴³⁴ Note that the per gallon cost is relatively insensitive to capacity, but is very sensitive to the amount of reduction required.

5. PROCESS MODIFICATIONS

If it is desired to remove soluble organic material, a pretreatment with activated carbon is necessary.¹⁶⁴⁸ This will also remove insoluble materials which might otherwise clog the membranes. To maintain a desir-

TABLE 3¹⁶⁴⁸

CAPITAL AND OPERATING COSTS FOR
TOMGD ELECTRODIALYSIS PLANT

<u>Amortization of Capital</u>	<u>¢/1000 Gallons</u>
\$1,830,000; 20 years at 5%	4.0
<u>Operation and Maintenance</u>	
Chemicals	4.4
Membrane replacement	3.3
Maintenance materials	0.9
Power	1.9
Labor	2.5
	13.0
TOTAL	17.0

Assumptions: 1. Influent TDS = 700 mg/l, effluent TDS = 450 mg/l
 2. Membrane life = 5 years
 3. Water recovery = 90%

TABLE 4¹⁶⁴⁷OPERATING COST FOR 28,000 GPD ELECTRODIALYSIS
UNIT AT COALINGA, CALIFORNIA*

	Cents per Thousand Gallons
Labor	16.67
Chemicals	6.25
Parts and replacements membranes	23.25
Filters	18.61
Other parts	3.01
Power	21.46
Amortization of capital investment	54.00
Total cost	143.25

*These figures include an allocation of existing labor time--none was added for this operation. Increased power cost and shorter filter life contribute slightly to the apparent high figure and straight line amortization on an investment of \$105,000 was used. A decrease by as much as 15 cents per thousand gallons is indicated by increased filter and membrane life. Potable water costs \$7.05 per thousand gallons before installation of the electrodialysis unit.

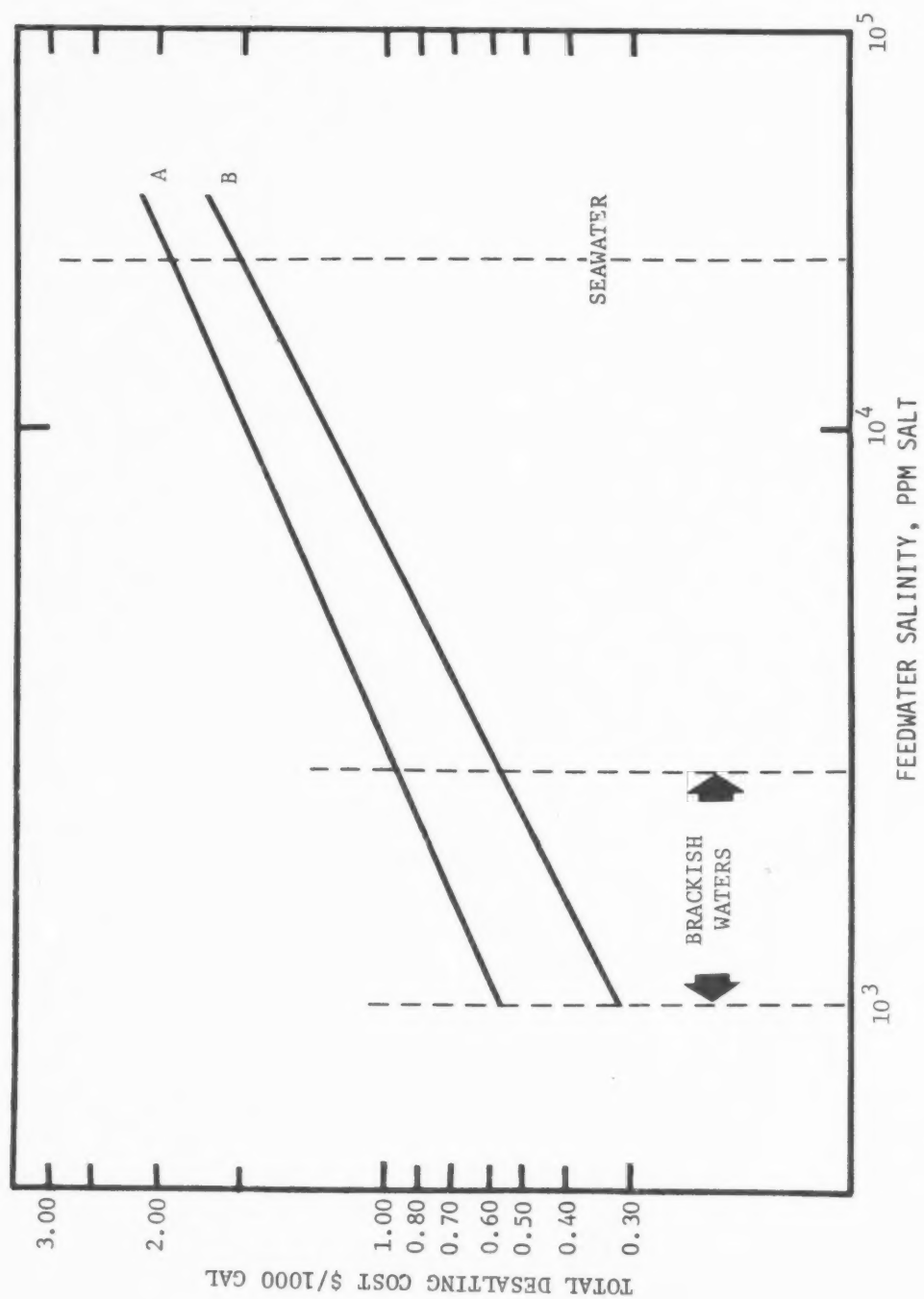


Figure 2. Water desalting cost vs feed water salinity for A, 100,000 gal/day capacity; B, 1,000,000 gal/day capacity. Product water assumed to contain 500 ppm salt.

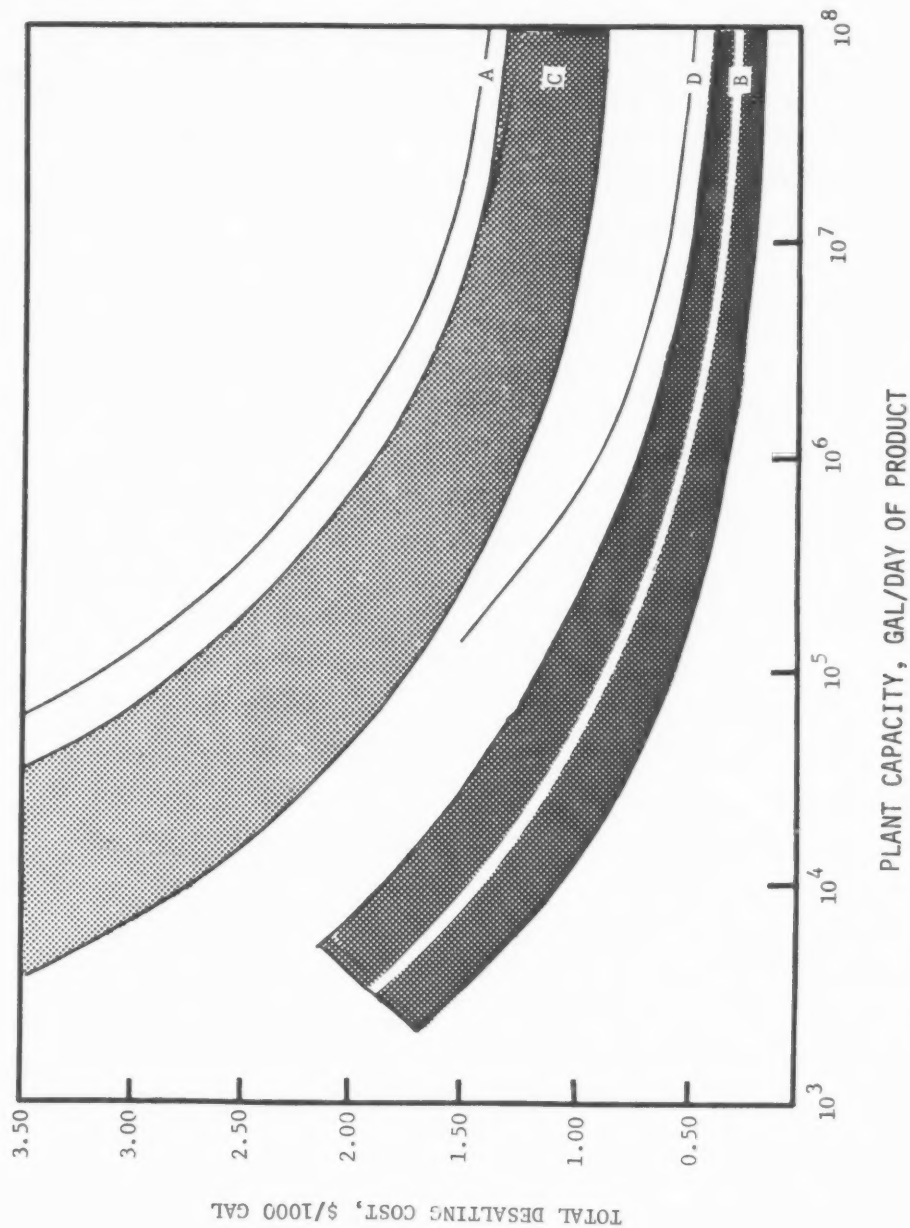


Figure 3. Water desalting cost as a function of plant capacity. Comparison of electrolysis for A, 35,000 500 ppm salt; B, 2000 500 (or 1000 150) ppm salt, the center line for that band representing the statistical average; C, 1962 estimates for various distillation processes; D, 1964 estimates of combined power generation and seawater distillation by multistage, multieffect distillation.

able pH of 3.5, the Los Angeles Sanitation Districts add sulfuric acid to the feed stream.

Ionics, Inc.,^{1650,1651,1652} a large manufacturer and installer of electrodialysis plants, suggests electrodialysis for reduction from thousands to hundreds of ppm followed by ion exchange to reduce the TDS to a final, acceptable level. While this approach may be efficacious under some circumstances, e.g., in making brackish water into high quality potable water, it is generally more expensive than reverse osmosis.

6. PROCESS APPLICABILITY

Electrodialysis is applicable when it is desired to separate out a variety of ionized species from an unionized solvent such as water. In this regard, it might prove advantageous over reverse osmosis, where different species may interfere with one another, or dialysis, where the relative diffusivities and activities of the species play an important role. Ionizable nitrates and phosphates (e.g., $\text{Pb}(\text{NO}_3)_2$, $\text{Hg}(\text{NO}_3)_2$, Na_3PO_4) are removed with varying degrees of efficiency. The Los Angeles County Sanitation Districts remove as much as 50 percent of the nitrates (as nitrogen) with a one-stage pilot plant (Figure 4 and Table 5).¹⁶⁴⁸ This plant was recently shut down because its 34 percent TDS removal was non-competitive on a cost basis with the higher removal efficiencies associated with reverse osmosis and ion exchange. Also, electrodialysis was found to be ineffectual for the removal of organic materials.

Electrodialysis has been used by military bases and other small communities for the production of marginally potable water (500 ppm TDS) from brackish water.^{1651,1652,1433,1646}

With regard to National Disposal Sites, electrodialysis is applicable for the treatment of waste streams where it is desirable to reduce the concentrations of ionizable species in the intermediate range (10,000 ppm to 500 ppm) over a broad range of pH (e.g., pH 1 to 14). Such streams may derive

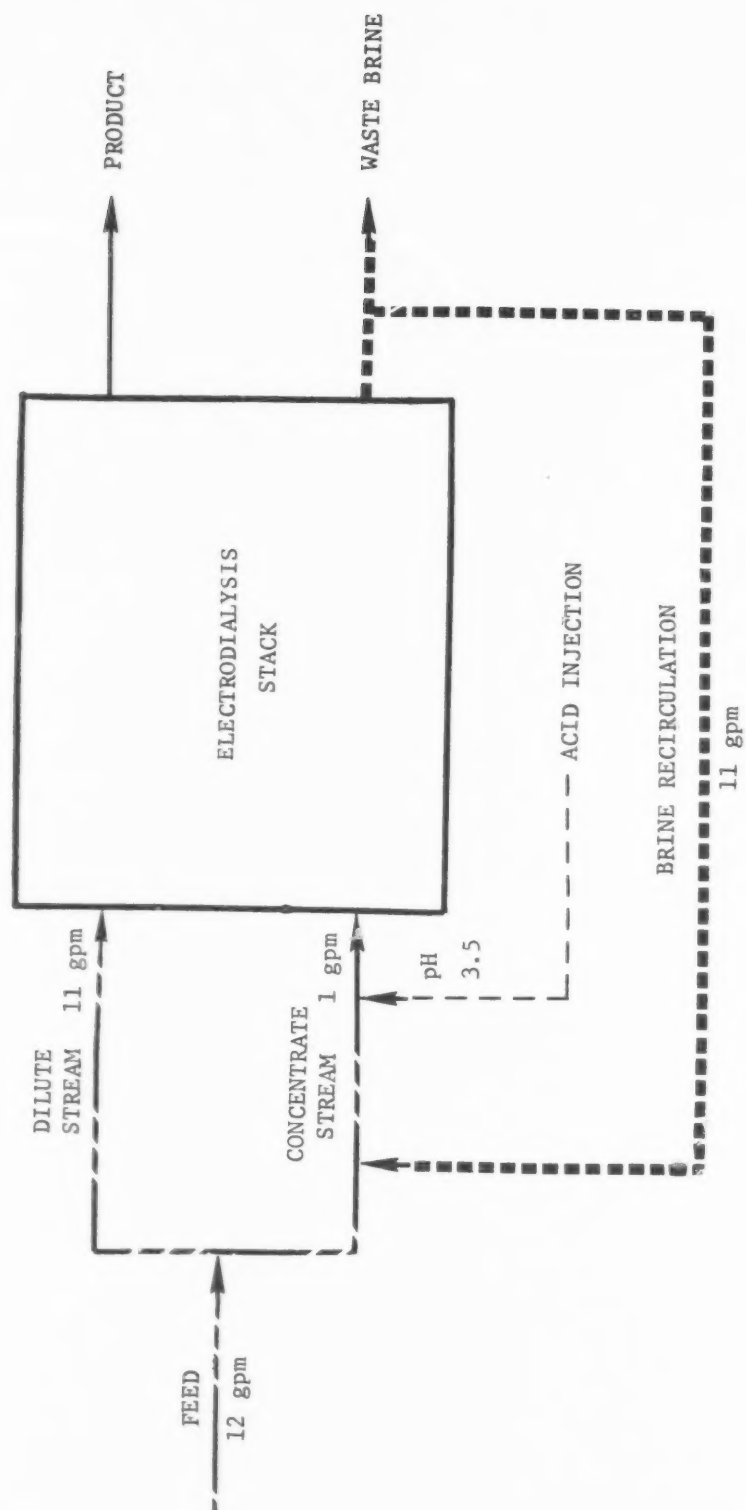


Figure 4. Schematic Flow Diagram of Electrolysis Pilot Plant

TABLE 5
WATER QUALITY CHARACTERISTICS OF ELECTRODIALYSIS PROCESS

TEST (mg/l)	INFLUENT	EFFLUENT	% REMOVAL
COD	9.4	8.0	14.9
NH ₃ -N	9.0	5.1	43.4
NO ₃ -N	6.2	3.1	50.0
PO ₄ -P	10.1	7.8	22.8
TDS	705.0	465.0	34.0

NOTES

1. 15,000 GPD Pilot Plant
2. Influent is Carbon Effluent
3. Averages Based on 10 Samples
4. Analyses Run on 24-Hour Composite Samples
5. Average Water Recovery = 83 Percent

directly as combustor scrubber liquors, for example, or they may be the effluent from another treatment process which handled a stream of much higher concentration (e.g., dialysis). If an effluent of concentration lower than 500 ppm is desired, the electrodialysis effluent could be fed into another treatment process such as ion exchange. Its applicability to unionized organic species is effectively nil.

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ION EXCHANGE

1. INTRODUCTION

Ion exchange may be defined as the reversible interchange of ions between a solid and a liquid phase in which there is no permanent change in the structure of the solid. It provides a method of separation useful in many chemical processes. Ion exchange is a method of collecting and concentrating undesirable materials from waste streams.

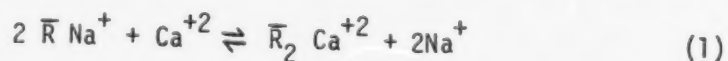
The mechanism of ion exchange is chemical, utilizing resins that react with either cations or anions. A waste treatment system may use a cation-exchange resin, an anion-exchange resin, or both types of resins, depending on the ions to be removed from the waste stream.

There are basically two types of ion-exchange operations - fixed bed and continuous countercurrent exchangers. In recent years the continuous ion exchanger has been used to reduce dilution, increase operating efficiency, and reduce operating cost.

In recognition of this current industrial trend and since the design considerations and underlying operating principles are essentially identical for both the countercurrent and fixed-bed systems, this report will emphasize the continuous operation (Figure 1).

2. OPERATION PRINCIPLE

The great utility of ion exchange rests with the ability to use and reuse the ion-exchange materials. For example, in water softening:



The exchanger $\bar{R}$ in the sodium ion form is able to exchange calcium with an

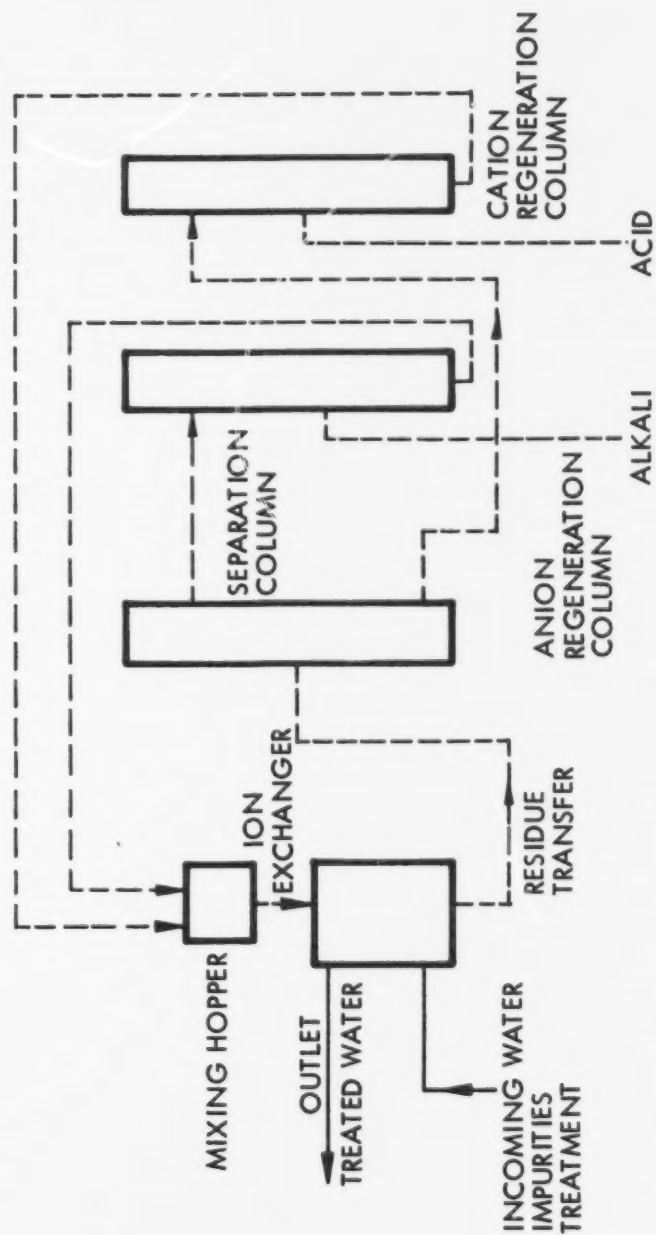


Figure 1. Continuous Ion Exchange Process - Mixed Bed

equivalent quantity of sodium. Subsequently, the calcium-loaded resin may be treated with a sodium chloride solution, bringing it back to the sodium form, ready for another cycle of operation. This conversion step is commonly called regeneration. The reaction is reversible and the resin is not permanently changed.

To be generally useful, an ion-exchange material must meet a certain number of basic requirements:

- (1) The material should have a high total capacity (a high degree of ionic substitution).
- (2) The resin should be structured chemically to exhibit good equilibrium characteristics when handling the expected solutes. It should be designed for operation in the proper pH range and with a degree of selectivity sufficient for the purpose and capable of regeneration.
- (3) Kinetic properties (determined by the nature of functional groups and backbone structure) should be such that a high operating or equilibrium capacity may be attained.
- (4) Extremely low solubility. Not only is the low solubility important for reuse but, inasmuch as the usual application of ion exchange is to remove impurities, the leaching of materials from the resin would have an adverse effect on the quality of the product.
- (5) Good chemical stability. This includes resistance to attack by an acid or base, oxidation or reduction, and radiation.¹⁴³³

The speed with which ion exchange takes place determines the portion of the equilibrium capacity which may be utilized in a practical dynamic situation. In column operations, rates determine the extent of deviation from the theoretical elution curve.

The rate of ion exchange depends, like ordinary adsorption, upon rates of the following individual processes: (1) diffusion of ions from the bulk liquid to the external surface of an exchanger particle; (2) inward diffusion of ions through the solid to the site of exchange; (3) exchange of the ions; (4) outward diffusion of the released ions to the surface of the solid; (5) diffusion of the released ions from the surface of the solid to the

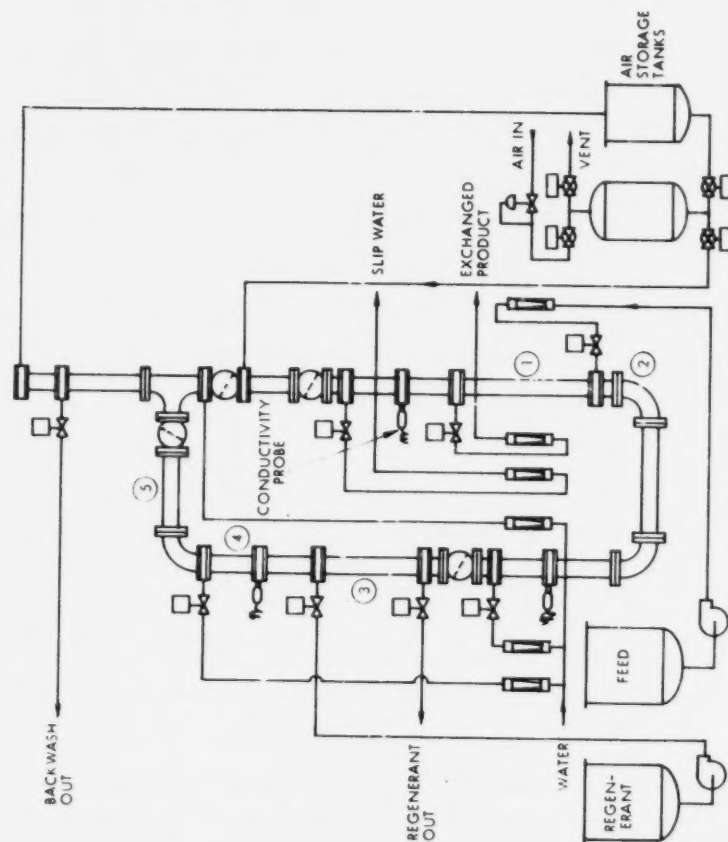
bulk of the liquid. In some instances, the kinetics of the exchange reaction (3) may be controlling, but in others the rate of reaction is apparently very rapid in comparison with the rate of diffusion. The diffusion rates can be described by appropriate mass-transfer coefficients.¹⁴³³ For those cases where the exchange reactions are rapid in comparison with the rates of mass transfer, the methods of design for conventional adsorbers may be applied to ion exchange operations directly.

3. PROCESS DESIGN

The "continuous countercurrent ion exchange system" is a closed system in which ion exchange resin moves from process section to process section in a batchwise manner. In this way a fresh quantity of resin is available for exchange with the waste stream almost all of the time, not being available only during the times the "slugs" of resin are moved from section to section. The three activities required for use and reuse of the resin, direct exchange, regeneration, and cleaning are accomplished in five process sections: 1) the service or loading section; 2) the service rinse section; 3) regenerant section; 4) regeneration rinse section and 5) backwash section (Figure 2).

The service section of a continuous ion exchange system is the primary working section of the apparatus. It is here that the resin is contacted with the waste stream and the specific ions exchanged. The material to be processed is fed into the service section and flows countercurrent to the direction of resin movement allowing complete utilization of the resin.

One of the important considerations in the design of the service section is resin selection. The ion exchange operating capacity, ionic selectivity, particle size, and hydraulic characteristics of the resin are factors which affect the design of the service section. The regeneration efficiency, resistance to attrition, and structural properties of the resin determine how often it must be replaced in the system.



1. Service or loading section
2. Service rinse section
3. Regenerant section
4. Regeneration rinse section
5. Backwash section

Figure 2. Flow pattern of a continuous countercurrent ion exchange system

The length of the ion exchange zone and the residence time of the resin must be determined for the design of the service section. These are dependent on the process ion exchange rate and the quantity of ions required to be removed from the waste stream.

The pressure requirements of the process liquid pumping system and the available pressure drop are determined from the design of the service section.

The method of moving the resin from one process section of the apparatus to another is an important design consideration. Compressed air is used to push a "slug" of resin and the "slip water" associated with it from one section to the next. The ratio of "slip water" to the amount of resin moved is kept at a minimum to increase resin productivity. This is usually accomplished by installing a conductivity probe in the service section of the apparatus. This probe senses the conductivity of the solution in the service section and electronically controls a valve which discharges the "slip water" from the system. If the conductivity of the solution is too high or too low, in relation to a certain "set" conductivity, the discharge valve is opened or closed accordingly.

The service rinse section rinses the resin free of the exchanged product before it leaves the service section. The rinse flows countercurrent to resin movement (as does the feed material) and can be controlled by conductivity. With a proper "slip water" ratio, the service rinse will be at a minimum and will not cause any appreciable dilution of the product.⁰³⁰⁴

When the resin is exhausted the compressed air, which is introduced above the service section, moves the resin into the regenerant zone of the apparatus. In this section, to obtain maximum utilization of the regenerant, the regenerant also flows countercurrent to the resin movement. The cation resins are regenerated with acid and the anion resins with caustic. The materials used in the construction of the regenerant section must be resistant to the corrosive properties of the regenerant.

Rinsing of the regenerated resin is accomplished by introducing a rinse into the apparatus above the point of regenerant introduction. The amount of regenerant rinse used is again controlled by conductivity to insure that the resin leaving the section is rinsed free of regenerant.

As the resin leaves the regenerant rinse section, it enters the backwash section. In this section, the resin receives its final rinse before returning to the service section of the apparatus.

The process liquid flow rate for a continuous ion exchange system is six to eight gpm/sq ft of resin surface area. The normal operation time of the system is two minutes in service and six seconds in resin movement, with three to five seconds needed for delays to insure proper valving sequence. With service flows operating 95 percent of the time, decreased resin volumes are possible.

Comparing a continuous system to a fixed bed system utilizing the same regenerant level, a capacity of 350 g/cu ft is obtained from a continuous ion exchange unit compared to 268 g/ cu ft for a fixed bed system. Final exchanged product dilution from a fixed bed is 28 percent, whereas in the continuous system it is 17 percent.⁰³⁰⁴

4. PROCESS ECONOMICS

The capital investment costs of ion exchange plants are dependent on the total volume of waste treated and, to a large extent, on the amount of total dissolved solids (TDS) removed. These costs range from \$850,000 for a 0.5 million gpd plant to \$9.5 million for a 10 million gpd plant (influent TDS of 1500 mg/l). For an influent TDS of 3000 mg/l the capital costs range from \$1.25 million for a 0.5 million gpd plant to \$10 million for a 5 million gpd plant.¹¹⁸²

The operating costs (less depreciation) for ion exchange plants are largely determined by the regenerant chemical costs which are in direct proportion to the rate of electrolyte removal. The operating costs for

a 0.5 million gpd plant (influent TDS of 3000 mg/l) total 35.0¢/1000 gal broken down as follows:

Labor	1.1¢
Materials	1.4
Chemicals	31.2
Utilities	<u>1.3</u>
Total	35.0¢

5. PROCESS MODIFICATIONS

The only major process modification currently in use is that of resin pretreatment for the purpose of adsorbing certain nonionic organic substances from a waste stream. This modified process is called ion exclusion and can be carried out with ordinary ion exchange resins. The resin is presaturated with the same mobile ions (cations or anions, depending on resin type) as are in the solution. It will then repel the ionic components of the solution, while adsorbing neutral non-aqueous materials such as alcohols, carboxylic acids, and ketones of relatively low molecular weight.

6. PROCESS APPLICABILITY

Ion exchange technology has been available and has been employed for many years for removing objectionable traces of metals and even cyanides from the various waste streams of the metal process industries. Objectionable levels of fluorides, nitrates, and manganese have also been removed from drinking water sources by means of ion exchange technology. Dangerous levels of radioactivity have been controlled by ion exchange devices and technology has been developed to the extent that the contaminants that are removed and concentrated can either be recycled or readily transformed into a harmless state or safely disposed.

Ion exchange technology can be employed to remove, concentrate, and immobilize all of the metallic and non-metallic ionic species listed by the United States Public Health Service as toxic or undesirable when present in concentrations above certain levels. There are, for example, ion exchange techniques for removing the following potentially undesirable species from water and waste streams; iron, aluminum, manganese, copper, zinc, chromium, silver, nickel, cobalt, cadmium, barium, uranium, radium, mercury, lead, fluorine, boron, nitrates, phosphates, arsenic, sulfides, phenol, chlorophenols, glucose, and glycerine.⁰⁶⁰⁹

It has been reported that an acid mine-drainage water containing 3,000 ppm of dissolved solids has been successfully processed to yield a water of quality suitable for industrial, agricultural, and domestic purposes by using a modification of the DESAL process (Figure 3). The process is based upon the use of an anion exchange resin, which functions in the bicarbonate cycle to treat the acid mine-drainage water. The effluent water is aerated and subsequently clarified to give a water of useful quality. The composition of the treated and untreated water (Table 1) is based on data supplied by Rohm and Haas Company.⁰⁶⁰⁹

A large (500,000 gallons per day) modified DESAL process plant will be operating late in 1972 treating acid mine-drainage effluents from the coal mining areas in Phillipsburg, Pennsylvania. The treated effluent will be used as a source of potable water for the local community.

With regard to National Disposal Sites, ion exchange could be used in conjunction with other processes as is done in the modified DESAL facility. The main purpose of ion exchange at the Site would be to concentrate and remove specific hazardous wastes from various waste forms prior to long-term storage or recycling.

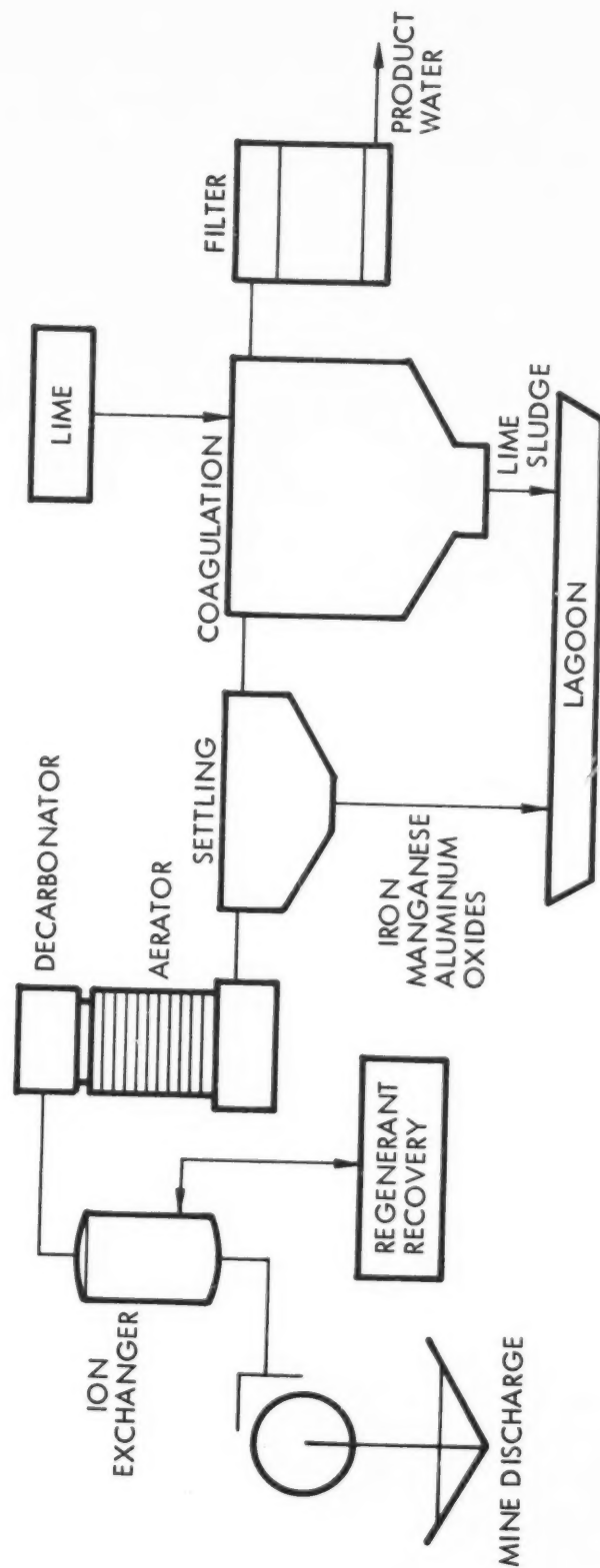


Figure 3. Acid Mine-Drainage Treatment Plant (DESAL Process)

TABLE 1
COMPOSITION OF UNTREATED AND DESAL--PROCESS TREATED
ACID MINE WATER⁰⁶⁰⁹

Constituent	Concentration, ppm (CaCO ₃)	
	Untreated	Treated
pH	3.1	8.5
Ca	964.0	290.0
Mg	480.0	10.0
Fe	895.0	<0.1
Al	556.0	<0.1
Mn	91.0	<0.1
SO ₄ ⁼	3104.0	100.0
HCO ₃ ⁻	--	200.0

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WASTE DISPOSAL PROCESS DESCRIPTOR REVERSE OSMOSIS

1. INTRODUCTION

Osmosis is the physical transport of a solvent across a membrane boundary, where the driving force for the transport is the difference in the solvent activities on either side of the membrane. Such a membrane is semi-permeable, i. e., it permits solvent molecules to pass through it, but is impermeable to solute species (Figure 1)¹⁴⁴¹. Solvent will diffuse through the membrane until its thermodynamic activity is equal on both sides. This activity is a function of the solvent concentration and the pressure head. The pressure head present at equilibrium is defined as the osmotic pressure.

If external pressure is applied to the side of less solvent concentration (Figure 2),¹⁴⁴¹ solvent will flow in the opposite direction. This is defined as reverse osmosis. This allows solvent to be extracted from a solution, so that the solution is concentrated and the extracted solvent is relatively pure. This idea is being exploited commercially in various areas of water purification, such as the purification of acid mine waters,⁰⁸⁵¹ tertiary sewage treatment,¹⁴³⁸ and the purification of tap water in the microelectronics industry.¹⁴³⁶ Often feed streams are subject to a reverse osmosis stage prior to passing through an ion exchange stage (Figure 3).¹⁴⁴¹

2. OPERATING PRINCIPLES

The basic consideration in the operation of any reverse osmosis unit is the amount of solvent material which can be passed through the membrane in a given time. This solvent flux across the membrane is proportional to the difference between the applied pressure and the osmotic pressure, or

$$J_w = A(\Delta P - \Delta \pi) \quad (1)$$

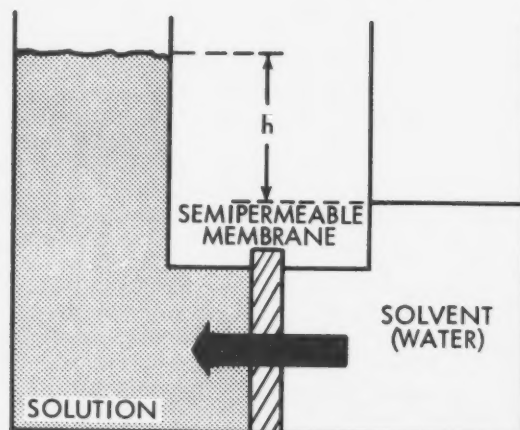


Figure 1. Osmosis; Normal flow from low to high concentration.

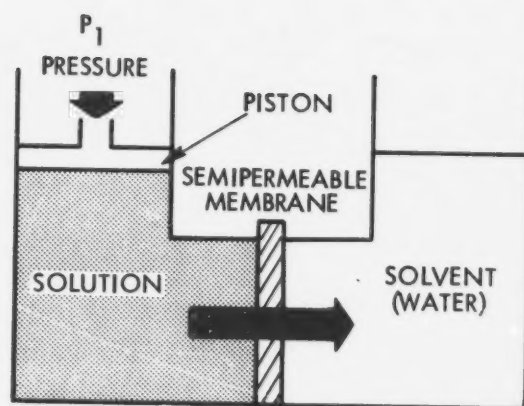


Figure 2. Reverse Osmosis; flow from high to low concentration.

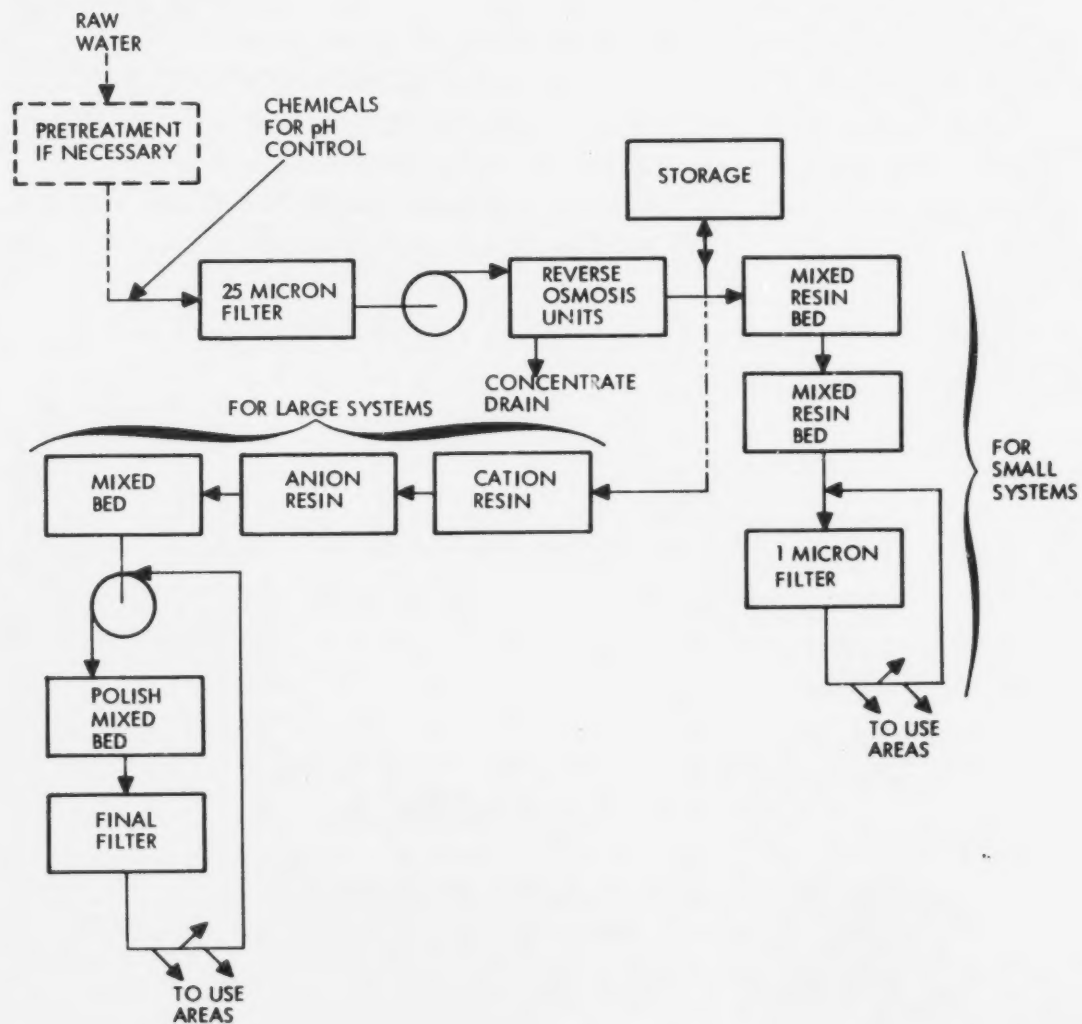


Figure 3. Flow Diagram of a Deionization System Incorporating Reverse Osmosis

where A is a constant related to the properties of the membrane, ΔP is the difference between the feed and product pressures, and $\Delta \pi$ is the difference between the osmotic pressure of the feed and product, respectively, with respect to pure water.

The *sin qua non* of the reverse osmosis process is the membrane. The exact mechanisms of membrane transport are not well understood, but two basic membrane operating principles are possible in theory:¹⁴³³ (1) a porous membrane which depends upon the size difference between water molecules, the typical solvent, and hydrated ions to impede the flow of the hydrated ions through the micropores, while allowing the smaller water molecules through, and (2) a diffusive, homogeneous membrane which cannot be described in terms of pore size, but which relies on physical and chemical differences between water molecules and hydrated ions in a poorly understood way to allow the selective passage of one and not the other.

The diffusive, homogeneous membrane is far more efficient and is used almost exclusively. Its characteristics impose the following qualitative rules of thumb in the operation of any reverse osmosis unit:¹⁴⁴¹

- (1) The passage of ions (failure to reject) will depend on the concentrations in feed and product;
- (2) The fraction of ions passing through is relatively independent of concentration at low concentration, i.e., when the mole fraction of solvent is almost 1.0;
- (3) Univalent ions pass more easily than multivalent ions;
- (4) Organic molecules of large molecular size will be rejected very efficiently;
- (5) Organic molecules of small molecular size will pass through quite easily.

3. PROCESS DESIGN

The process design is concerned with improving the factors associated with maximizing the solvent flux (Eq. 1) and prolonging the membrane lifetime.

The solvent flux, J_w is directly proportional to the pressure differential, $\Delta P - \Delta \pi$. $\Delta \pi$ is dependent on the characteristics of the feed stream and is generally raised approximately one psi for every 100 ppm dissolved solids in the feed stream. ΔP is limited by the pressure which the membrane can withstand, and currently is limited to 600 psi in commercially installed units. ^{1436,0851} Gulf General Atomic, ^{0851, 1437} which is presently conducting research and development in this field while installing units on a commercial basis has successfully operated experimental units at 800 psi and now talks of 1500 psi as possible.

The membranes currently in use commercially and experimentally are made of cellulose acetate modified in various ways. They are developed and manufactured by the basic chemical companies, DuPont, Dow, Kodak, etc. and further modified, packaged, and sold in reverse osmosis systems by several firms, including Polymetrics, Inc. and Gulf General Atomic, Inc. Mills ¹⁴⁴¹ describes the membranes as provided by the manufacturers:

"The modified cellulose acetate membranes, which are in general use, are about 100 microns thick. The active part of the membrane is a dense layer 0.2 to 1.0 micron thick formed during the initial stages of the gelling or precipitation of the membrane. This thin active layer forms the rejection surface of the membrane and its properties can be changed by: (a) the addition of additives to the casting solutions, (b) variations in the solvent and nonsolvent portions of the casting solutions, and (c) post-casting treatments. The remainder of the membrane is a porous mass which supports the active surface. Cellulose acetates can be characterized by their degree of acetylation (0 to 3); the grades of cellulose acetate which are preferred

for membrane preparation have a degree of acetylation of approximately 2.5; this corresponds to an acetyl content of approximately 40 percent".

Choosing a membrane is still primarily a state of the art procedure, involving extensive testing on the laboratory level up through several stages of pilot plant development. ^{1436,1437,1443, 1446} For this reason it is impractical to give generalized rules of thumb for membrane selection in this description.

These membranes have rejection efficiencies of 95 percent for univalent ions, 98 to 99 percent for multivalent ions, and 90 percent for organic molecules whose molecular weights exceed 100.

Since cellulose acetate hydrolyzes readily in strongly acidic or strongly basic solutions, the pH of the feed water must be kept between 3 and 8, and preferably between 5 and 7 (Gulf ^{0851,1437} reports several significant excursions with no ill effects). Sulfuric acid or caustic solution are commonly used to adjust the pH to appropriate values and facility for determining pH and metering in the solutions must be provided in the design.

The membrane constant, A, in Eq. 1, usually varies between 0.015 and 0.020 gal./ft²-day-psi at 70 F ^{1441,0851} and increases approximately 1.5 percent/F with temperature. A higher operating temperature is therefore preferred, but an upper limit of only 100 F is allowed in practice, because the membrane is subject to hydrolysis above this temperature. Membranes are subject to fouling caused by sedimentation, precipitation, and bacteria. Gulf ⁰⁸⁵¹ and McDonnell Douglas ⁰⁷⁸² have successfully combated fouling in experimental systems by running solutions of common household detergents through the system.

The packaging of membranes to conserve space and maximize longevity has achieved considerable sophistication. Tubular, spiral, and hollow fiber configurations have been used successfully and are under vigorous

investigation.^{1436,0782,1446} Packaging efficiencies as high as 1,500 ft² of membrane in a cylinder 4 in. in diameter by 4 ft. in length are already available commercially with a membrane guarantee for 1 year.¹⁴⁴⁶ With a membrane constant of 0.02 gal./ft²-day-psi and a pressure differential of 600 psi, such a unit could treat over 15,000 gpd.

In addition to the membrane assembly, a pressure vessel to contain the membrane is required along with pumps and suitable instrumentation. Polymetrics¹⁴⁴⁶ supplies an 18,000 gpd unit with associated equipment in a volume of 12 ft by 4 ft.

4. PROCESS ECONOMICS

For the past several years, Gulf General Atomic^{0851, 1437} has been operating a pilot plant at Norton, West Virginia for recovery of acid mine waters. Sufficient data has been gathered to allow a realistic assessment of the capital and operating costs associated with such a venture. These costs may be regarded as typical for reverse osmosis plants for the purposes of this description since details such as chemical additives to the feed water to adjust pH, the addition of bactericides, etc. comprise a small fraction of the total cost. Capital costs are estimated at approximately \$780,000 for a 1,000,000 gpd unit. Operating costs for a plant of this size total 41.3¢/1,000 gal., broken down as follows:

Power	7.5¢
Chemicals	3.2¢
Operation and Maintenance	5.0¢
Membrane Module Replacement	25.6¢
TOTAL	41.3¢

5. PROCESS MODIFICATIONS

Modifications for the most part consist of doctoring the feed stream with additives to improve the rejection rate and inhibit membrane fouling. This is still considered to be an art rather than a science and reverse osmosis unit manufacturers do a considerable amount of tailor-made development work with every unit they sell.^{1436,1437} The membrane manufacturers, of course, concentrate on improving membrane properties and longevity, and in concert with the unit manufacturers, strive to improve the packing techniques for greater rejection and acceptable pressures.

Often, preliminary laboratory investigations indicate that several dissolved substances in a waste stream may be mutually incompatible for efficient reverse osmosis treatment. This then requires a change of membrane or preliminary separation of the offenders prior to the reverse osmosis treatment.

6. PROCESS APPLICABILITY

Almost any dissolved solid can be treated by reverse osmosis, providing the concentrations are not too high (Table 1) and it is practical to adjust the pH to range 3-8.¹⁴⁴⁰ The main problem is membrane specificity for particular species, as influenced by the presence of other species, pH, tendencies toward fouling, additives, etc. when concentrations are high. Reverse osmosis units capable of handling a wide variety of substances of relatively high concentration simultaneously or in series are somewhat beyond the present state-of-the-art,^{1436,1439} although systems can be designed for handling limited combinations of species. Typical commercial reverse-osmosis units have capacities of 15,000 gpd and normally include a prefilter and pH control pump in the integrated system (Figure 4).

At present several reverse osmosis pilot plants are in operation. For example, Gulf General Atomic, Inc.^{1437,1438,0851} has set up two pilot plants of approximately 10,000 gpd feed water capacity - one in Norton, West Virginia to process acid mine waters being deposited in Grassy Run Creek and one in Pomona, California under a project jointly sponsored

TABLE 1
MEMBRANE REJECTIONS AND PERMISSIBLE FEED WATER CONCENTRATIONS

Name	Symbol	Typical % Reject.	Maximum Allowable (%) Concentration in Feed Water
Sodium	Na ⁺	94-96	3-4
Calcium	Ca ²⁺	96-98	*
Magnesium	Mg ²⁺	96-98	*
Potassium	K ⁺	94-96	3-4
Iron	Fe ²⁺	98-99	*
Manganese	Mn ²⁺	98-99	*
Aluminum	Al ³⁺	99	5-10
Ammonium	NH ₄ ⁺	88-95	3-4
Copper	Cu ²⁺	96-99	8-10
Nickel	Ni ²⁺	97-99	10-12
Strontium	Sr ²⁺	96-99	—
Hardness	Ca and Mg	96-98	*
Cadmium	Cd ²⁺	95-98	8-10
Silver	Ag ⁺	94-96	*

ANIONS			
Chloride	Cl ⁻	94-95	3-4
Bicarbonate	HCO ₃ ⁻	95-96	5-8
Sulfate	SO ₄ ²⁻	99	8-12
Nitrate	NO ₃ ⁻	93-96	3-4
Fluoride	F ⁻	94-96	3-4
Silicate	SiO ₂ ²⁻	95-97	—
Phosphate	PO ₄ ³⁻	99	10-14
Bromide	Br ⁻	94-96	3-4
Borate	B ₄ O ₇ ⁴⁻	35-70**	—
Chromate	CrO ₄ ²⁻	90-98	8-12
Cyanide	CN ⁻	90-95**	4-12
Sulfite	SO ₃ ²⁻	98-99	8-12
Thiosulfate	S ₂ O ₃ ²⁻	99	10-14
Ferricyanide	Fe(CN) ₆ ³⁻	99	8-14

* Must watch for precipitation, other ion controls maximum concentration.

**Extremely dependent on pH; tends to be an exception to the rule.

ORGANICS:

	Molecular Weight		
Sucrose sugar	342	100	25
Lactose sugar	360	100	25
Protein	10,000 Up	100	10-20
Glucose	198	99.9	25
Phenol	94	***	—
Acetic acid	60	***	—
Lactic acid	90	***	—
Dyes	400 to 900	100	—
Biochemical Oxygen Demand (BOD)		90-99	—
Chemical Oxygen Demand (COD)		80-95	—
Urea	60	40-60	Reacts similar to a salt
Bacteria & virus	5,000-100,000	100	—
Pyrogen	1000-5000	100	—

***Permeate is enriched in material due to preferential passage through the membrane.

GASES, DISSOLVED:

Carbon dioxide	CO ₂	30-50%
Oxygen	O ₂	Enriched in permeate
Chlorine	Cl ₂	30-50%

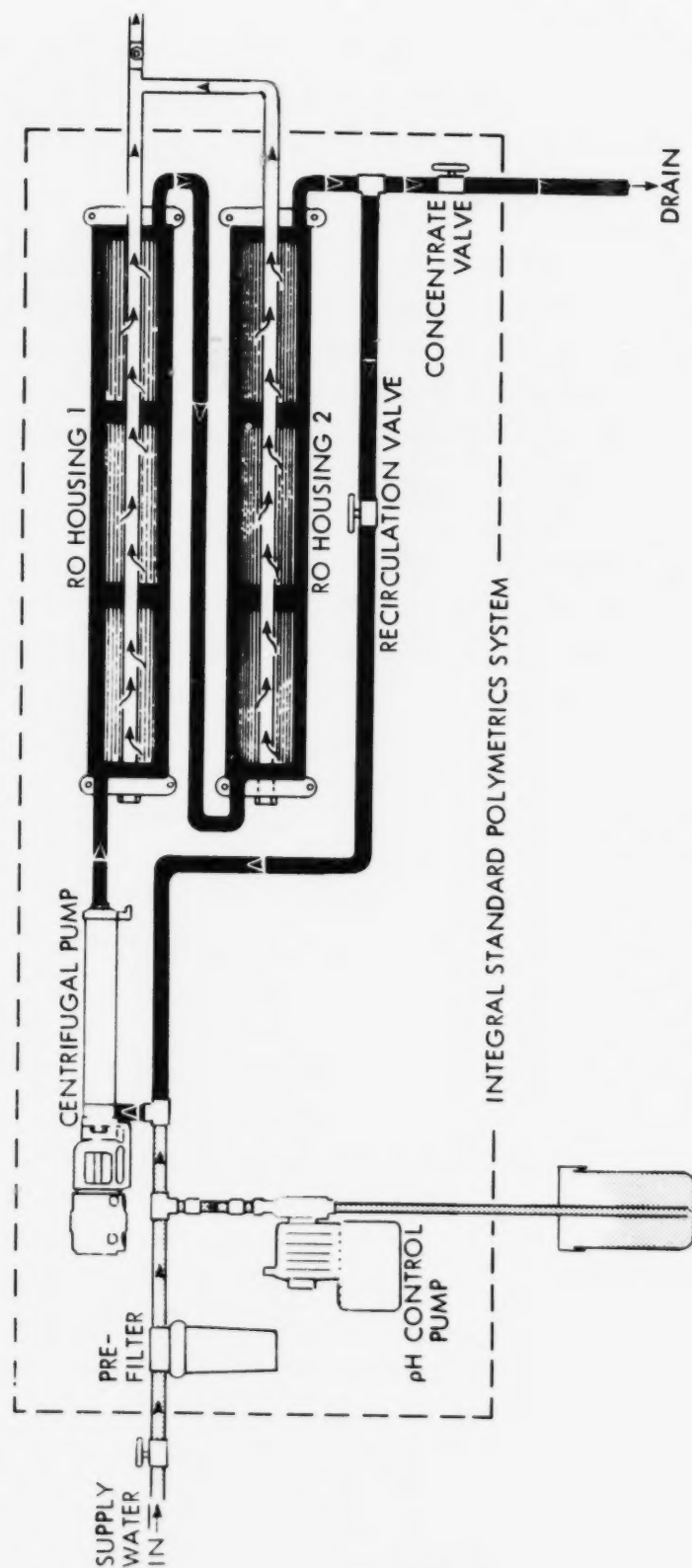


Figure 4. Typical, Commercially Available Reverse Osmosis Unit 1439, 1446

by the Los Angeles County Sanitation District and the U.S. Environmental Protection Agency. The purpose of the Pomona facility is to investigate the feasibility of reverse osmosis as a tertiary sewage treatment process to remove salts from industrial waste waters.

Results are available for the Norton plant for a 54-day test in 1969.⁰⁸⁵¹ The plant was run at 600 psi with a 75 percent recovery, i.e., 3 gal. pure product out of every 4 gal. feed water. Average rejection was 97.6 percent of an initial feed water concentration of 3,600 ppm. The unit was in continuous operation 85 percent of the time, with most of the down time attributable to pump malfunction.

The Pomona operation may be summarized as follows:¹⁴³⁸ 13,000 gpd feed water from an activated sludge secondary sewage treatment contain 700 mg/l dissolved inorganic solids. As a pretreatment, 90 percent of the organic matter is removed by carbon adsorption. The product water contains 30 mg/l dissolved solids. The data obtained to date suggest that ion exchange is more economical than reverse osmosis, which in turn is more economical than electrodialysis. However, ion exchange is ineffectual in the removal of viruses, and if reverse osmosis can be shown to be effective for virus removal, it might prove the better choice. It is expected that reverse osmosis has excellent rejection for viruses, since they are of very large molecular weight.

Reverse osmosis is an appropriate method for concentrating wastes on the hazardous materials list which form ions in aqueous solution, e.g., ammonium chromate. Also, organic materials of large molecular weight, such as dyes or bacteria, which dissolve or form suspensions in water are readily separable. Materials whose rejections by reverse osmosis are very poor are mainly low molecular weight organic compounds which do not ionize in aqueous solution, e.g., ethanol or urea. Of course, as a general rule, materials which are marginally soluble or insoluble are not appropriate, since their precipitation clogs the membrane.

With regard to National Disposal Sites, reverse osmosis could be used for concentrating scrubber liquors, as might originate from combustors. The waste could then be further concentrated by evaporation, for example, prior to long-term storage or recycling to the supplier.

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RADIOACTIVE WASTE SOLIDIFICATION

1. INTRODUCTION

The solidification of high-level liquid radioactive wastes is utilized as a pretreatment for storage or disposal. Solidification results in the conversion of the liquid waste to solids to provide greater safety during handling, transportation, and disposal. The increased safety associated with the solid wastes compared to the liquid is because the solid form is less mobile, less soluble in water, smaller in volume, and more rugged physically.

Several different processes have been developed for solidifying radioactive wastes. Generally, these processes are broken down into two categories. They are high-level and intermediate-level radioactive waste solidification processes, and low-level waste solidification processes.

The high-level solidification processes are used for the solidification of the waste generated by reprocessing the spent fuel from nuclear power plants. The spent fuel is in the solid form when it is removed from the reactor and shipped to a reprocessing plant where it is processed for the recovery of the usable fissionable materials. The high-level waste is the aqueous effluent of the reprocessing solvent extraction operation. The incentive to reprocess the spent fuel is three-fold: a need to prevent depletion of the present uranium stocks; the economic benefits realized which can represent a savings of approximately \$38,000 per metric ton of fuel processed; the need to isolate and concentrate the fission product waste.⁰⁵⁵¹

Solvent extraction using nitric acid as a salting agent is the means currently used for the first-stage removal of the fissionable materials. The resultant high-level wastes are primarily aqueous solutions of inorganic nitrate salts. Any differences in the waste streams generated

will mainly occur due to variations in the amount and type of salts added to the solutions during reprocessing. These variations can have a marked impact on the solidification process conditions and on the nature of the final product.

In the United States four processes have been developed for the solidification of high-level wastes. They are pot calcination, spray solidification, phosphate glass solidification, and fluidized bed calcination. Basically, in each of these four processes heat is applied to raise the temperature of the waste to drive off the volatile constituents that will eventually cool to a solid. In some of these processes chemicals are added to the waste stream to reduce the melt temperature to below 1,200 C. In all these processes, additional gas and vapor streams are generated which require additional processing.

The intermediate-level wastes which are obtained from evaporating second- and third-cycle wastes, cell and equipment decontamination, solvent cleanup, and off-gas scrubbers will generally be treated the same as high-level wastes. The volume of these wastes range from 200 to 500 gal. per metric ton of fuel processed. These wastes are principally nitrate solutions of sodium, potassium, aluminum, and iron, and often contain sulfate, fluoride, and phosphate in addition. Their activity levels are generally less than a tenth of a curie per gal. The low-level waste solidification processes are adaptable to a number of different types of waste streams. These include wastes generated at nuclear power plants and fuel reprocessing facilities, along with the wastes resulting from research laboratories and medical and industrial applications of radioisotopes. The wastes generated at nuclear power plants include radioactive filter sludges, spent resins, and wastes which result from the treatment of the condensate water and water from other sources in the plant. The low-level wastes from the only operating fuel reprocessing plant is contained in a liquid stream and contains only very small quantities of fission products which are well below the Maximum Permissible Concentrations (MPCs) listed in 10CFR20.

2. OPERATION PRINCIPLE

Solidification of radioactive wastes is based on the principle of converting the wastes from a mobile aqueous state to a solid state to reduce the mobility of radionuclides after burial or storage. The process for the solidification of the high-level radioactive wastes is based on the addition of heat to volatilize the water, leaving a melt that will eventually cool to a solid. To lower the waste melt temperature and to enhance the solidified product, chemical modification of the waste composition is required. Generally, compositions for waste solidification require the addition of at least 70 mole percent of inert chemicals to incorporate the wastes into a low temperature melt (less than 1,000 C).

3. PROCESS DESIGN

This section is divided into two parts. In the first part the desired characteristics of the solidified waste product are discussed. These characteristics are of primary importance in evaluating the adequacy of the solidification processes. In the second part the design of the solidification processes for the high-level and low-level wastes is described.

Solidified Waste Characteristics

The purpose of any solidification process is to achieve a substantial increase in the safety associated with the handling, storage, transportation, and disposal of radioactive wastes. The increase in the safety of the solidified waste is a result of the reduction in the mobility of the radionuclides contained in the waste. To assess the safety of any disposal technique, it must be recognized that solidification is only part of the total disposal scheme. The other important consideration is the type of disposal method utilized.

Leachability. A low leachability of the solidified waste is required to minimize the release of radioactivity to the environment in the event that the waste container is breached and water should come in contact with the solidified waste. The ideal leach rate of the solidified waste can be assessed in terms of the specific activity of the radionuclides present and their MPC values in water.²¹⁴⁹ The ideal leach rate is determined as follows:

$$L. R. = \frac{(MPC)}{(S.A.)} \cdot \left(\frac{V}{T}\right) \cdot \left(\frac{1}{A}\right)$$

where

- L.R. = leach rate, gm/cm² - day
- MPC = maximum permissible concentration of radionuclide in water, curies/cm³
- S.A. = specific activity of radionuclide, curies/gm
- V = volume of water contacted, cm³
- T = time of contact, days
- A = area of waste contacted, cm²

To provide an indication of the ideal leach rate assume one square centimeter of solidified waste were contacted by one thousand cubic centimeters of water for one minute. This is equivalent to a flowrate of 0.264 gallons per minute. For a waste containing only Sr⁹⁰ with a specific activity of 142 curies/gm and a 168 hour MPC value of 1x10⁻¹² curies/cm³ the leach rate of the solidified waste should not exceed 1x10⁻⁸ gm/cm² - day. Since the ideal leach rate is a function of the area of waste contacted, which decreases with time, the maximum allowable leach rate would increase with time.

Stability. The stability of the solidified waste is important to assure that the basic structure and properties of the waste remain intact. The degree to which these properties change is a measure of the stability of the waste. The basic structure and chemical properties of the waste will change due to the decay of the radioactive materials to other chemical elements. This effect is especially pronounced for reactor produced waste since approximately 30 percent of the fission products present

after 6 months out of the reactor will eventually decay to other chemical elements. Since the change in the chemical composition of the waste is impossible to prevent, the wastes should be held a sufficient time before solidification to allow a majority of the short-lived isotopes to completely decay. The exact time the waste should be held before solidification is a function of the half-life of the radionuclides present and should be such that any changes in the solidified waste composition will not affect its basic structure or physical properties.

The exposure of the wastes to high levels of radiation can cause radioactive gas evolution, swelling and discoloration of the waste, and changes in its leach rate and physical properties. The exposure rate and its effect on the solidified waste are dependent upon the type of waste and amount of radioactive material contained. The level of radiation damage is usually determined experimentally. Once the level of damage is determined the amount of radioactivity or the amount of radioactive material contained in the waste should be kept below the level at which significant damage occurs.

The temperature stability of the waste determines the maximum temperature at which the waste can be exposed before gas formation and dispersion occurs. Generally, gas formation from solidified wastes is not significant if the waste temperature does not approach processing temperature.⁰⁷¹⁵ For some of the high-level solidification processes, a few exceptions have been indicated for calcine from feeds with high sodium nitrate content (nitrogen oxide volatility) and for some phosphate-sulfate melts (sulfur oxide volatility).⁰⁷¹⁵

Thermal Conductivity. The maximum temperature of the solidified waste must be maintained below prescribed limits to prevent the waste from melting or vaporizing. To achieve these limits, a high thermal conductivity is required to minimize the temperature rise between the center and outer surface of the waste. The temperature difference between the center and outer surface of a solid cylinder of self-generating heat varies as:

$$\Delta T = \frac{1}{K} \cdot Q \cdot D^2$$

where ΔT = temperature difference
 K = thermal conductivity
 Q = heat rate per unit volume
 D = diameter of cylinder

Thus, a higher thermal conductivity will linearly decrease the temperature at the center of the waste and increase the amount of self-generating heat that can be included in the waste. In addition, a higher thermal conductivity also increases the size of the storage container and allows for a decrease in the specific volume (liters/gram) of the solidified waste.

Process Description

High-Level Waste Solidification Processes. Four processes have been developed for the solidification of high-level wastes. They are pot calcination, spray solidification, phosphate glass solidification, and fluidized bed calcination. The pot, spray, and phosphate glass processes have been demonstrated on a full scale, engineering level by Battelle-Northwest at Richland, Washington. 0715, 0716, 0717, 0527, 0732 The fluidized bed process has been demonstrated in a large capacity plant 0694, 0711 by Idaho Nuclear Corporation at Idaho Falls, Idaho. A description of each solidification process is attached (Figures 1 and 2) and basically, in each of these four processes, heat is applied to raise the temperature of the waste to drive off the volatile constituents, leaving a solid. Generally, chemicals are added to the waste stream to: (1) reduce the melt temperature; (2) prevent the release of volatile components; and (3) improve the properties of the final product.

Each of these processes generates additional gas and vapor streams which contain reduced but still toxic levels of radioactivity. To treat these waste streams for the removal of radioactivity, additional auxiliary processing equipment is required. The auxiliary processing system usually includes several separate cycles of evaporation plus

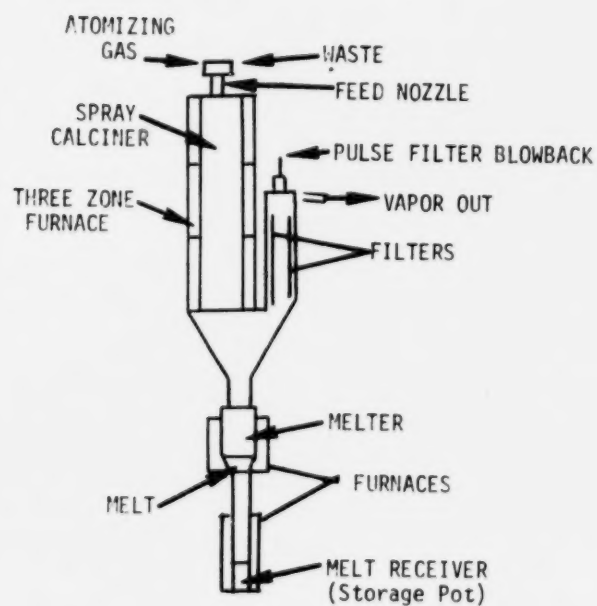
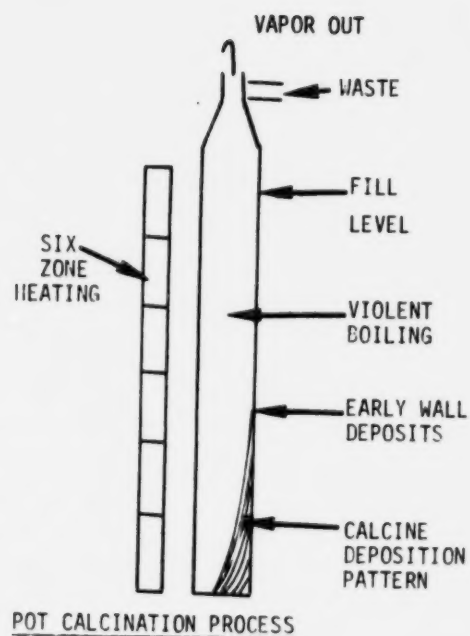
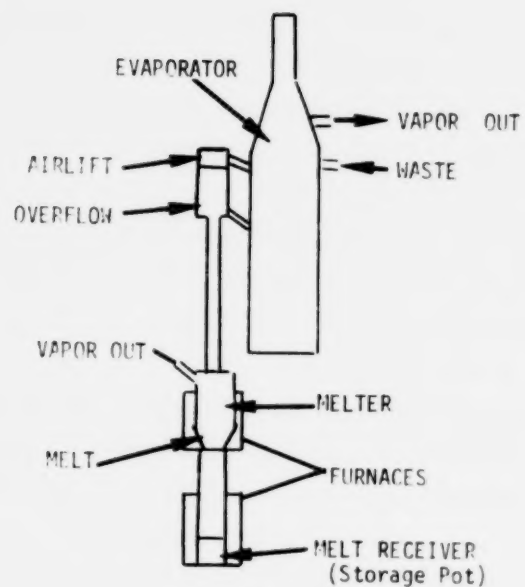
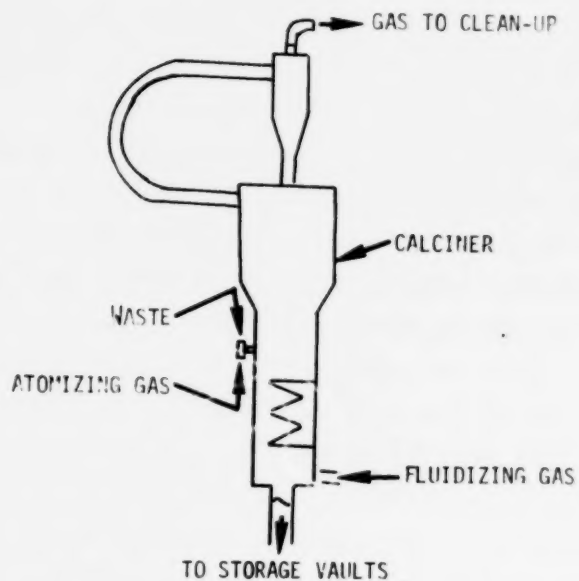


Figure 1. Pot calcination and spray solidification



PHOSPHATE GLASS SOLIDIFICATION



FLUIDIZED BED CALCINATION

Figure 2. Phosphate glass solidification and fluidized bed calcination

condensation followed by a stage of filtration. An acid fractionator is also employed for the removal of nitric acid. This system is followed by a caustic scrubber and further stages of filtration. Decontamination factors of 10^9 have been obtained with liquid effluents. 0716

The overall characteristics of the four types of solidified wastes are summarized (Table 1) and a brief description of the design of each process is presented below.

Pot Calcination. A batch process in which the processing vessel is also the final container for the solidified waste. In this process the liquid waste is added to the pot and heated in a multiple-zone furnace. As the waste is heated, scale forms on the wall of the pot. The scale grows in thickness until all the waste in the pot has been calcined and reaches a temperature of 850 to 900 C. The pot is then cooled, sealed, and taken to storage. The only major requirement for additives to the liquid waste stream is for the retention of the volatile components. The overall cycle capacity with a 12-inch-diameter pot is 14 liters/hr which represents an equivalent waste processing capacity of 0.90 tonnes/day.

The basic elements required for the design of the equipment in pot calcination are: a multiple-zone furnace for heating and cooling, a pot to calcine the waste, and an off-gas line from the pot that can be continuously washed down. The multiple-zone furnace must be designed to provide different heating regions along the vertical portion of the pot. Six zones for a pot filled with 6 ft of calcine have been found to be adequate. 0715 The pots are made of corrosion resistant material to survive the severe corrosion conditions during processing. Three-hundred-series stainless steel, generally 304L or 310, has been found to be adequate. 0716 Continuous washing of the off-gas line from the pot is required to prevent plugging by entrained calcine or sludge. The continuous washing can be accomplished by condensing the vapors formed in the line.

TABLE 1
CHARACTERISTICS OF HIGH LEVEL SOLIDIFIED WASTE⁰⁷⁰⁵

	Pot Calcination	Spray Solidification	Phosphate Glass	Fluidized Bed
Form	Calcine Cake	Monolithic	Monolithic	Granular
Description	Scale	Microcrystalline	Glass	Amorphous
Hardness	Soft	Hard	Very hard	Moderate
Friability	Crumbly	Tough	Brittle	Moderate
Bulk Density, g/ml	1.1 to 1.5	2.7 to 3.3	2.7 to 3.0	1.0 to 1.7
Thermal Conductivity, watts/ m- C	.19 to .26	.87 to 1.73	.69 to 1.73	.17 to .43
Leachability, g/cm ² -day	10 ⁻¹ to 1	10 ⁻⁶ to 10 ⁻³	10 ⁻⁷ to 10 ⁻⁴	10 ⁻¹ to 1
Volume, liters/1000 Mhd (thermal)	1. to 2.5	1.2 to 3	1.5 to 5	1.5 to 5
Chemical Composition, mole %				
Fission product oxides	15 to 80	5 to 30	5 to 25	5 to 50
Inert metal oxides	10 to 50	40 to 50	10 to 30	10 to 90
Phosphorous oxides	~0	25 to 40	~60	~0
Maximum Stable Temperature, C	~900	Phase separation at ~900	Devitrifies at ~500	~600
Container Material	Stainless Steel	Mild or Stainless Steel	Mild or Stainless Steel	Mild or Stainless Steel

A major problem in the design of the pot calcination process is retention of volatile components such as sulfate, ruthenium, and mercury. Sulfate can be retained almost entirely in the calcine form by adjusting the ratio: 0716

$$\frac{\text{Chem. equiv. (alkali + alkaline earth metals)}}{\text{Chem. equiv. (nonvolatile anions)}} \geq 1.1$$

Chemical additives to meet this ratio are usually calcium or sodium nitrates. Since the above ratio also includes potentially volatile alkali metal oxides, the following ratio should also be met:

$$\frac{\text{Chem. equiv. alkali metals}}{\text{Chem. equiv. (nonvolatile anions)}} \leq 1$$

The volatilization of ruthenium can be decreased by the addition of phosphate or hypophosphate ions as phosphoric acid. The retention of mercury is difficult since it forms no compounds that are stable at temperatures greater than 600 C. The mercury should be removed prior to solidification by passing the waste through beds packed with copper or aluminum. The copper beds are not feasible if the acid concentration of the waste is greater than 0.5 M.

Spray Solidification. A continuous process in which the liquid waste is fed through an atomizing nozzle into a heated calcine tower. The water is evaporated, dried, and the waste is calcined to a powder as it falls through the calciner tower. It then falls into a melter where it is melted at temperatures of 800 C to 1,200 C. The melt in the melter flows through an overflow weir to a storage pot which is then cooled and sealed. Process gases flow into the adjacent filter chamber where the calcined powder collects as dust on the porous metal filters. The dust is periodically blown off by sudden pulses of high pressure steam or air and falls back into the melter with the main powder stream. The overall cycle capacity is approximately 20 liters/hr of liquid.

The basic elements required for the design of the equipment in spray solidification are: an atomizing nozzle; a multiple-zone furnace; an off-gas cleaning system; a continuous melter and furnace;

and a receiver pot and multiple-zone furnace. The atomizing nozzle is designed to break the feed up into small droplets (80 to 100 microns diameter) to permit drying and to calcine the feed. Commercial internal-mixing nozzles have proved satisfactory.⁰⁷²⁵ The multiple-zone heater in the spray calciner is designed to maintain the temperature in the spray tower higher than the walls of the spray tower to prevent sticking to the tower walls. The calcine dust in the off-gases can be separated by porous stainless steel filters with an average pore size of 65 microns and a total area of 1 sq ft/(liter)/(hr) of feed to the calciner.⁰⁷²⁵ The continuous melter which is positioned below the calciner to collect the powder must withstand the effects of corrosion and high temperature (up to 1,200 C). Platinum is the only known reliable material for the melter at the present time. Other materials such as a chromium-alumina cermet and an alloy of 50 percent chromium-50 percent nickel are being examined. The receiver pot and multiple zone furnace designs are similar to those in pot calcination.

In spray solidification the feed composition has a strong effect on its performance. Additives are required so that a melt-forming matrix is formed which is stable at high temperatures. Phosphate is generally used as the melt former. The melt temperature limits are adjusted using a phosphate flux with an overall cation-to-phosphate ratio (M/P) of 2 to 3.⁰⁷²⁵ In this relationship, M is the total metal ion equivalent and P is the total molarity of phosphorous present. The melt temperature increases with the M/P ratio approaching 1,000 C at a M/P ratio of 3.

Sulfate and ruthenium are the two principal products most easily volatilized. The sulfate is retained in the melt by the addition of calcium which combines chemically with the sulfate. The ruthenium volatility is reduced by the elimination of the melt-making flux from the feed and the addition of all the melt-making flux to the melter.

Phosphate Glass Solidification. A continuous glass solidification process which is carried out in three steps: feed preparation; low temperature denitration-evaporation; and high temperature glass forming. The feed preparation involves the addition of glass-forming chemicals to the liquid waste. The liquid waste which contains all the melt-making additives is first fed to an evaporator where it is concentrated into a thick phosphate slurry. This slurry is fed to a continuous melter where the material is heated to 1,000 to 1,200 C to form a molten glass. The molten glass then flows into a storage pot which is cooled and sealed. The process capacity is limited by the melter which has a capacity of 10 to 12 liters/hr compared to the evaporator capacity of 35 liters/hr. 0718

The basic elements required for the design of the equipment are: a continuous denitrator-evaporator; a melter feed system; a continuous melter and furnace; and a receiver pot and multiple-zone furnace. The evaporator design must be capable of handling corrosive liquids, providing low hold-up volume and maximum suspension of solids. The evaporator is made of titanium and is constructed of a special design. 0732 The melter feed system is designed to pump and meter the waste flow between the evaporator and the melter. Special designs using either an airlift or slurry pump have been developed. The melter requirements are the same as those for the spray solidifier except that the heat transfer requirements are 50 to 100 percent higher. The receiver pot design is similar to that for pot solidification.

The chemical additives are added directly to the feed and consist mainly of orthophosphoric acid. To form a good quality glass, one mole of phosphate is required per mole equivalent of nonvolatile cation. 0732 If the ratio is less than one, a poor grade glass is formed and, if greater than one, the excess phosphate is evolved until the ratio is about one. If the mole percent of oxides of the alkali metals is less than half the total metal oxides in the melt, additional alkali metals (i.e., sodium nitrate) must be added to obtain a glass that forms at 850 to 1,000 C and has good handling properties.

In the evaporator about 0.5 to 1 percent of the ruthenium will volatilize but no appreciable sulfate or phosphate volatilization has occurred.⁰⁷¹⁶ In the melter the principal off-gases are water, nitrates, sulfate (when present in waste), and ruthenium. When sulfate is not present, the off-gases from the melter are combined with the off-gases from the evaporator, or condensed separately and recycled to the evaporator to reduce the overall off-gas activity. When sulfate is present, steam additions are required to help recover the sulfate and to prevent corrosion by diluting the condensate and reducing its temperature.

Fluidized Bed Calcination. A continuous process in which the liquid waste is converted to granular solids by heating in a fluidized bed of the granular solids. In this process the liquid waste is injected through an atomizing nozzle into the side of a heated bed (400 to 600 C) of granular solids. The bed is continuously fluidized by gas flowing upward through the bed. As the waste contacts the hot bed, it is evaporated and calcined as coatings of the bed particles. The bed particles are continuously removed from the calciner and transported to storage bins. The calcine material that is entrained with the process gases is removed from the gas stream by cyclone separators or filters and transported to the storage bins. About 60 percent of the solidified waste product is removed by the calciner and the remainder is removed during the processing of the off-gas stream. The overall cycle capacity is 180 to 260 liters/hour.

The basic elements required for the design of the equipment in the fluidized bed process are: an atomizing nozzle; a calciner and furnace; and an off-gas cleaning system to remove the calcine dust. The atomizing nozzle is designed to break up the feed into small droplets to permit rapid drying without caking. Commercial external-mixing pneumatic nozzles are used with a gas volume of 500 to 800 times the volume of the liquid feed.⁰⁶⁹⁴ Air or superheated steam is used for atomization. The calciner size is 3 to 6 times the hourly volume of liquid feed to the calciner and has a length-

to-diameter ratio in the range of 1.5:1 to 4:1. ⁰⁷¹⁵ The heat requirements for the calciner is one kilowatt for each liter per hour of liquid feed. The heat is provided by an in-bed heat exchanger through which sodium-potassium (NaK) circulates. The sodium is heated externally to about 740 C and circulated by an electromagnetic pump. The calcine dust in the off-gas stream is removed by the use of cyclones and porous stainless steel filters with periodic pulse blowback for on-line cleaning. The pulse blowback system is similar to the system used in spray solidification.

Additives to the feed solution are primarily required to retain the volatile components and not to enhance the final solidified waste product. Ruthenium volatility is reduced to about 1 percent when sugar is added to the feed. ⁰⁷¹⁵ Sulfate and fluoride is retained with the calcine (99%) and fluoride corrosion is controlled by the addition of calcium in stoichiometric equivalence to the amount of fluoride present. ⁰⁷¹⁵

Low-Level Waste Solidification Processes. Solidification processes have been developed for the incorporation of low-level radioactive wastes in asphalt, cement, and polyethylene. These treatment processes are fully described elsewhere ^{0547, 0697, 0704, 1017,} and will only be briefly described here. The treatment processes for each of the solidification processes is similar. The waste and the solidification material are added and mixed together in a predetermined ratio. This ratio depends on the type of waste involved. Studies have defined compositions of asphalt and polyethylene for incorporation in organic and inorganic waste streams. ⁰⁵⁴⁷ These compositions are attached (Table 2). Tests have resulted in a ternary operating diagram for the incorporation of filter sludge and ion exchange resins in cement. ⁰⁶⁹⁷ These results are also attached (Figure 3).

TABLE 2
ASPHALT AND POLYETHYLENE MATRIX COMPOSITION FOR ORGANIC
AND INORGANIC WASTES 0547

Waste	Composition, wt%		Filler	Comments on Project	
	Matrix	Material		At 160 C	At 25C
Organic					
25 (tributyl phosphate)	38 (asphalt)		37 (Attapulgate-150)*	Pours	Firm, but bleeds
25 (tributyl phosphate)	35 (asphalt)		40 (Grundite) ⁺	Pours	Soft and tacky
25 (tributyl phosphate)	37 (asphalt)		38 (Attacote) [†]	Pours	Firm, but bleeds
25 (tributyl phosphate)	37 (asphalt)		38 (Attacloy) [‡]	Pours	Soft and tacky
30 (tributyl phosphate)	70 (DYL polyethylene)		None	Fluid	Very good
30 (tributyl phosphate)	70 (DYDT polyethylene)		None	Very fluid	Good
30 (carbon tetrachloride)	70 (DYDT polyethylene)		None	Very fluid	Good
30 (tetrachloroethylene)	70 (DYDT polyethylene)		None	Very fluid	Good
Inorganic					
40 (NaBO ₂)	60 (asphalt)		None	Very fluid	Good
60 (NaBO ₂)	40 (asphalt)		None	Very fluid	Good
50 [Ca(BO ₂) ₂]	50 (asphalt)		None	Fluid	Good
55 [Ca(BO ₂) ₂]	45 (asphalt)		None	Fluid	Good
20 (NaBO ₂)	80 (DYL polyethylene)		None	Fluid	Good
30 (NaBO ₂)	70 (DYL polyethylene)		None	Fluid	Good
40 (NaBO ₂)	60 (DYL polyethylene)		None	Fluid	Good
20 (NaBO ₂)	80 (DYDT polyethylene)		None	Fluid	Good
40 (NaBO ₂)	60 (DYDT polyethylene)		None	Very fluid	Good

* Attapulgate-150: a magnesium aluminum silicate drilling clay produced by Minerals and Chemicals Philipp Corp.
⁺ Grundite: a high-strength bonding clay produced by the Illinois Clay Products Co.

[†] Attacote: a magnesium aluminum silicate coating clay produced by Minerals and Chemicals Philipp Corp.

[‡] Attacloy: a magnesium aluminum clay produced by Minerals and Chemicals Philipp Corp.

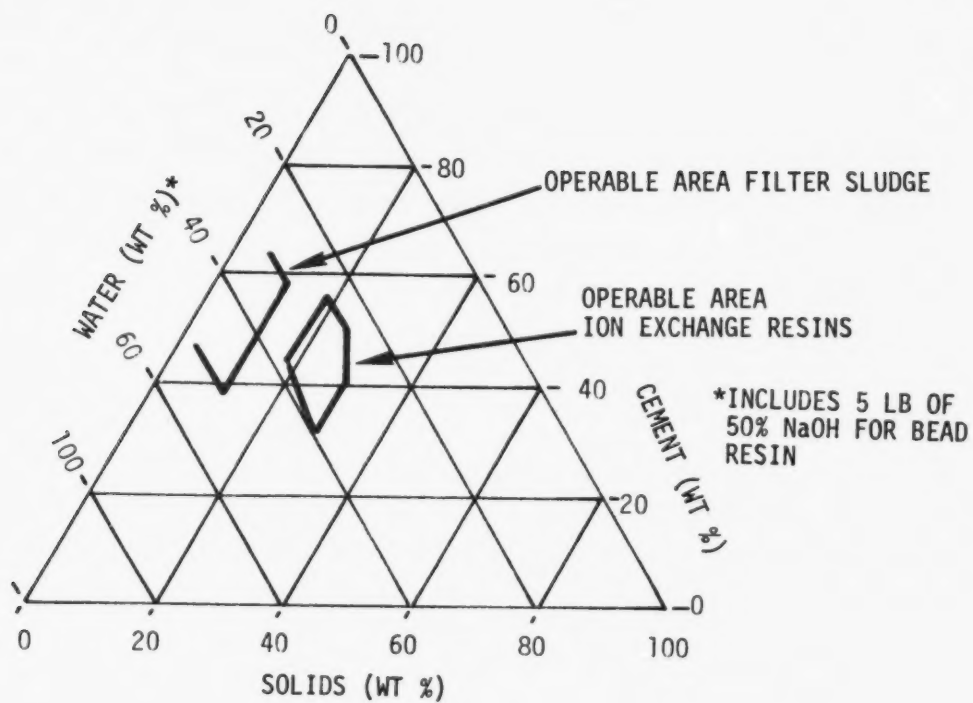


Figure 3. Cement solidification process ternary operating diagram for filter sludge and ion exchange resin wastes

The solidification process for asphalt and polyethylene consists of adding the waste to the asphalt or polyethylene in an evaporator with a wall temperature between 130 and 160 C. Mixing is accomplished by agitator paddles. The paddles turn with a downward forcing action that forces the mixture out the bottom and into the disposal container. In the solidification process for cement the waste and cement are generally mixed directly together in 55-gal. drums.

4. PROCESS ECONOMICS

For the four high-level solidification processes only cost studies for pot calcination were found to be available.⁰⁷⁰⁵ These cost studies were made using an economics model based on a discounted cash flow technique. This type of model requires that the income received must provide for the recovery of the investment by the establishment of a reserve account to pay all waste management operations that remain to be completed after all income has ceased. Using this model the costs of pot calcination were calculated as a function of the age of the waste and size of the storage container. These costs are presented for the case in which the center-line temperature of the waste is held at less than 900 C when standing in air (Figure 4). These costs ranged from \$4,200/metric ton of fuel for 1-year-old waste in 6-in.-diameter pots, to \$460/metric ton of fuel for 30-year-old waste in 24-in.-diameter pots.

Cost estimates for the incorporation of aqueous low-level waste in asphalt and polyethylene have been made.⁰⁵⁴⁷ These cost estimates were made using a price of \$0.015/lb for asphalt and \$0.20/lb for polyethylene. The total processing cost was \$0.34/gal. of waste for asphalt and \$0.80/gal. of waste for polyethylene.

5. PROCESS APPLICABILITY

The high-level waste solidification processes have been developed especially for the spent fuel wastes generated from nuclear power

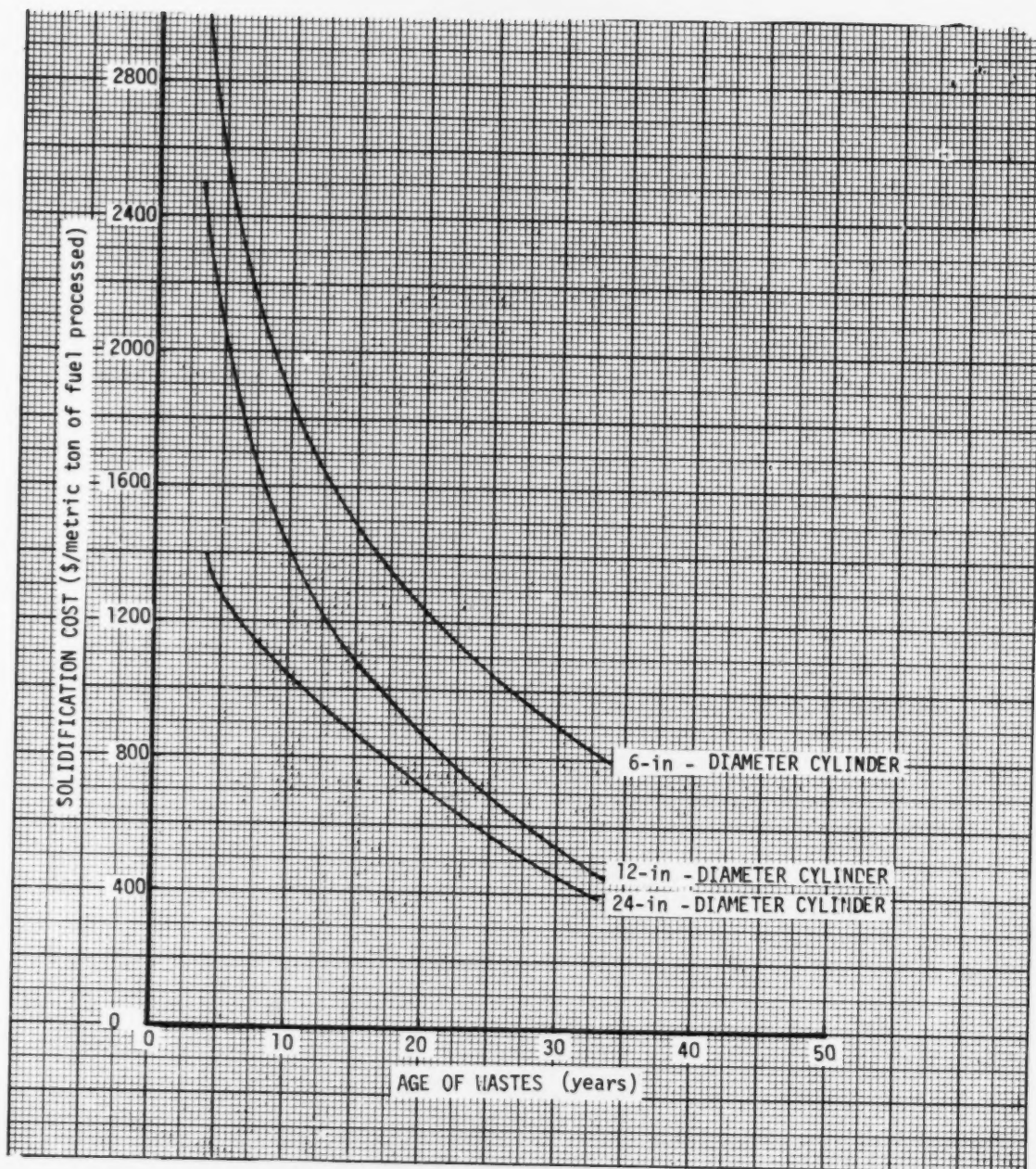


Figure 4. Pot calcination costs as a function of the age of the waste⁰⁷⁰⁵

plants. These wastes include the reactor-produced fission products as well as the actinides or transuranium elements.

Since these solidification processes result in a waste volume reduction their applicability to certain types of wastes can be limited by the waste heat generation rates. This is a problem not only for the wastes generated by the presently constructed thermal power reactors, but the size of this problem will increase with the introduction of the fast breeder reactors. To assess the magnitude of this problem calculations were made to determine the maximum allowable heat that would be stored in a particular storage container for each of the four solidification processes. The reactor-produced fission product heat generation rates are included as a function of time for both the current thermal power reactors and the proposed fast breeder reactors (Figure 5). The fast breeder reactor heat generation rates are approximately five to ten times higher than those of the current thermal power reactors.

The maximum container heat content was calculated assuming a maximum waste temperature of 900 C and a storage environment of 20 C air, which corresponds to a container wall temperature of approximately 450 C. For these conditions, the heat content of a cylindrical storage container is shown as a function of container diameter and waste thermal conductivity (Figure 6). Combining these data with those previously shown (Figure 5) the maximum heat content and corresponding age of the fission products (storage time before solidification) were determined for each of the four solidification processes. These data are presented for a 6-in.-diameter container (Table 3). For the present thermal power reactors the required age of the fission products or the storage time before solidification varied from 0.2 to 2.1 years and for the fast breeder reactors from 2.7 to 9.5 years. For an 8-inch-diameter container the required age for the breeder reactor would vary from 8.4 to greater than 10 yrs. These data were presented for storage in air and the age or storage time of the waste would be reduced if the containers were stored in water or in an enclosed, air-conditioned room. These data indicate that the waste heat content can limit the use of these solidification processes especially

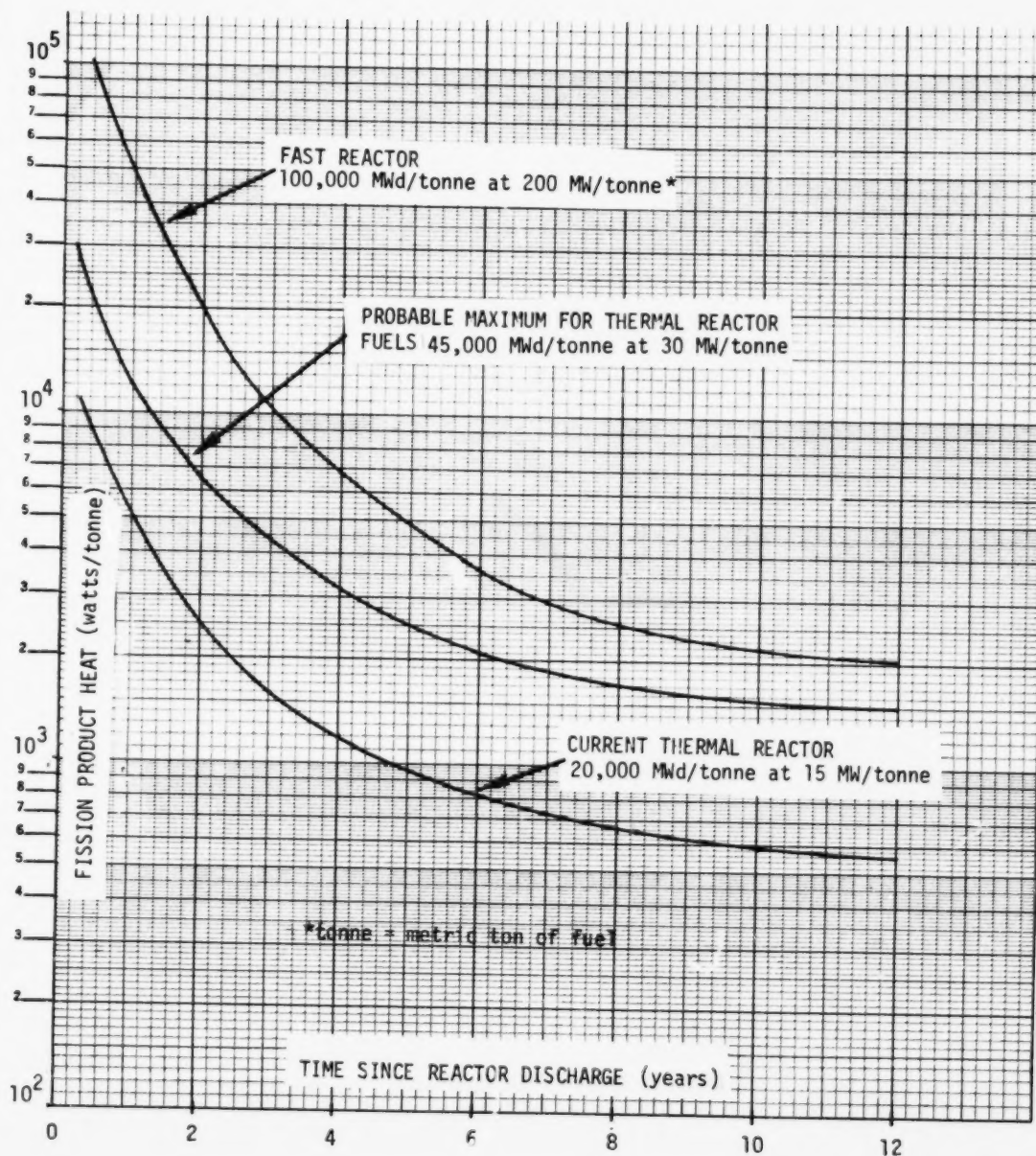


Figure 5. Fission product heat generation rates⁰⁷¹⁶

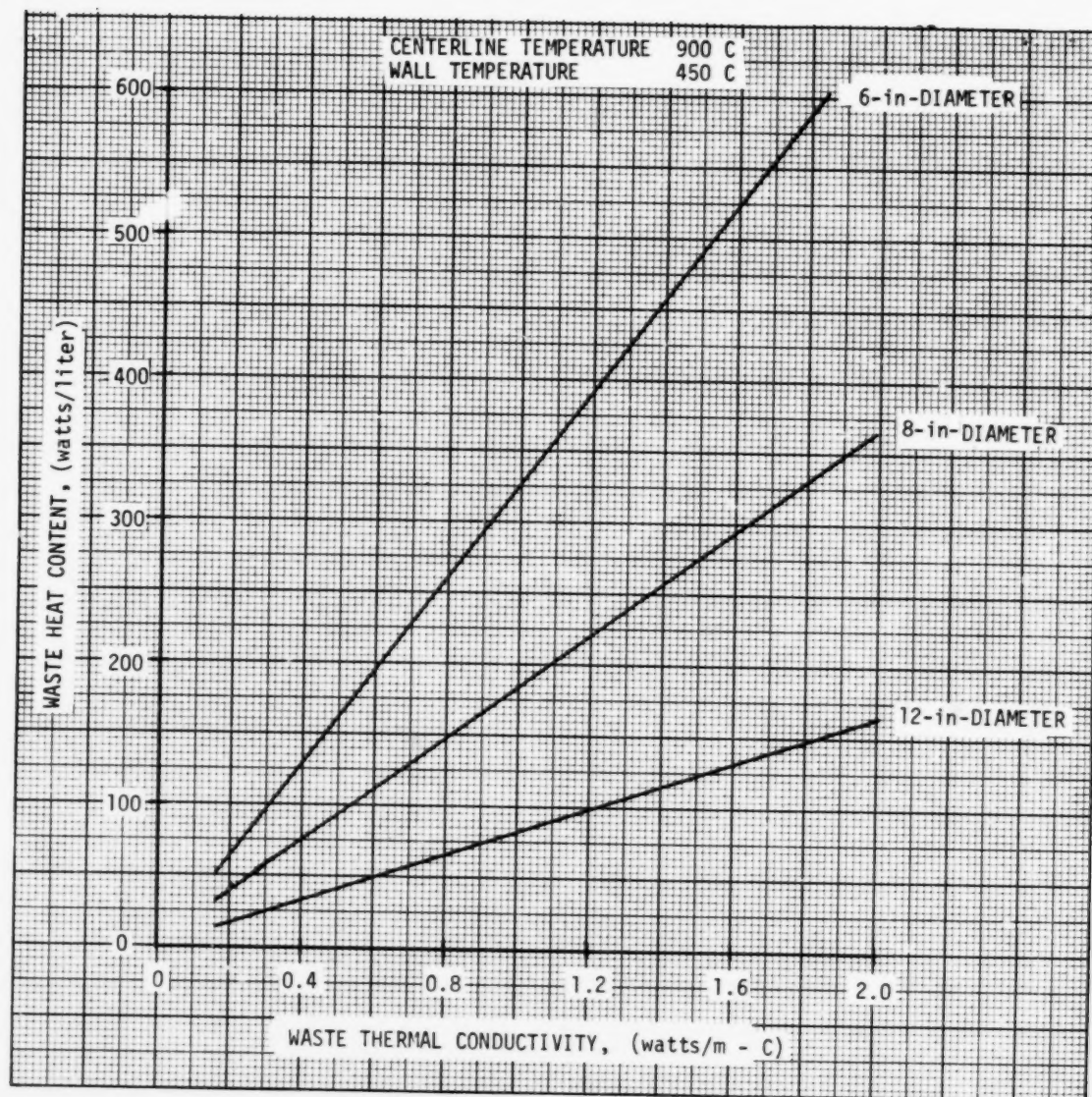


Figure 6. Waste heat content as a function of waste thermal conductivity and pot diameter

TABLE 3
ALLOWABLE HEAT CONTENT OF HIGH-LEVEL SOLIDIFIED WASTE

	Pot Calcination	Spray Solidification	Phosphate Glass	Fluidized Bed
Thermal Conductivity, watts/m- C				
Range	.19 to .26	.87 to 1.73	.69 to 1.73	.17 to .43
Average	.23	1.30	1.21	.30
Maximum Heat Content (6" Dia. Pot)				
Watts/liter	75	425	395	100
*Watts/metric ton of fuel	2250	12,750	11,850	3000
Age of Fission Products, years				
Current Thermal Reactor	2.1	.2	.2	1.7
Maximum Thermal Reactor	5.5	1.0	1.0	4.2
Fast Reactor	9.5	2.7	2.8	6.9

*Solidified Waste Volume = 30 liters/tonne

with the fast breeder reactor fuel wastes. To overcome this problem, several of the more active fission products such as Sr^{90} , Ru^{106} , Cs^{137} , and Ce^{144} may have to be removed from the waste prior to solidification.

A comparison of the four solidification processes is presented (Table 4). From the standpoint of process and flexibility, pot calcination is superior to the other three processes, but the other three processes are superior in terms of the solidified waste product. A comparison shows that spray solidification or phosphate glass solidification come closer to matching the desired characteristics of the solidified waste developed in Section 3. It must be recognized that solidification is only part of the total disposal scheme and that the final comparison or selection must be made in conjunction with the disposal method to be utilized.

The low-level waste solidification processes are applicable to those wastes that are disposed of by direct burial in the ground. In general, these solidification processes are more adaptable to the short-lived isotopes (6 months to 30 yr) and less hazardous materials. The source of these types of wastes are the secondary streams generated at nuclear power plants and fuel reprocessing facilities, along with the wastes resulting from research laboratories and medical and industrial applications of radioisotopes.

Cement, asphalt, and polyethylene are used for the solidification of these types of wastes. Cement products are only moderately insoluble compared to the asphalt and polyethylene products. The leach rates of asphalt and polyethylene products are 50 to 100 times lower than those of cement products containing similar amounts of waste salt. A comparison between a good asphalt product (about 60 Wt. % salts) and a good cement product (about 25 Wt. % salts) shows that the weight percent of Cs^{137} leached in 10 weeks from the cement product was 58 percent and from the asphalt product was 0.56 percent.

TABLE 4

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Cement can be used with almost all waste streams but the products formed are inferior to the asphalt and polyethylene products in terms of solubility. The integrity of the cement product also decreases greatly as the concentration of soluble salts increases.¹⁰¹⁷ When low concentrations of waste salts are used, the volume of the final cement product is much larger (60%) than the original waste volume. With asphalt products volume reductions of almost two have been obtained.⁰⁶⁹⁷ In addition, most operations with cement are dusty and cumbersome and good mixing is difficult to achieve.

In general, asphalt and polyethylene are better materials than cement for solidifying low-level wastes except for waste streams that contain significant amounts of oxidizing agents. Economically, asphalt is preferred to polyethylene since its processing costs are less. Asphalt is not recommended for wastes that contain high concentrations of oxidizing salts. Tests⁰⁵⁴⁷ have shown that mixtures containing relatively large amounts of nitrate or nitrite burn vigorously and that a mixture containing 65.6 Wt. percent nitrate (90 Wt. % NaNO_3) with a porosity of approximately 50 percent can be detonated with blasting gelatin. Polyethylene can probably be used with oxidizing salts, but further studies are needed to assess the safety of the system. For organic wastes polyethylene is recommended since a high percentage of the wastes can be accommodated without the use of an inert filler that is required with the asphalt-organic mixture.

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